THE OPEN UNIVERSITY
Science: A Second Level Course

BLOCK 3 IGNEOUS PROCESSES
phase relations and geochemistry

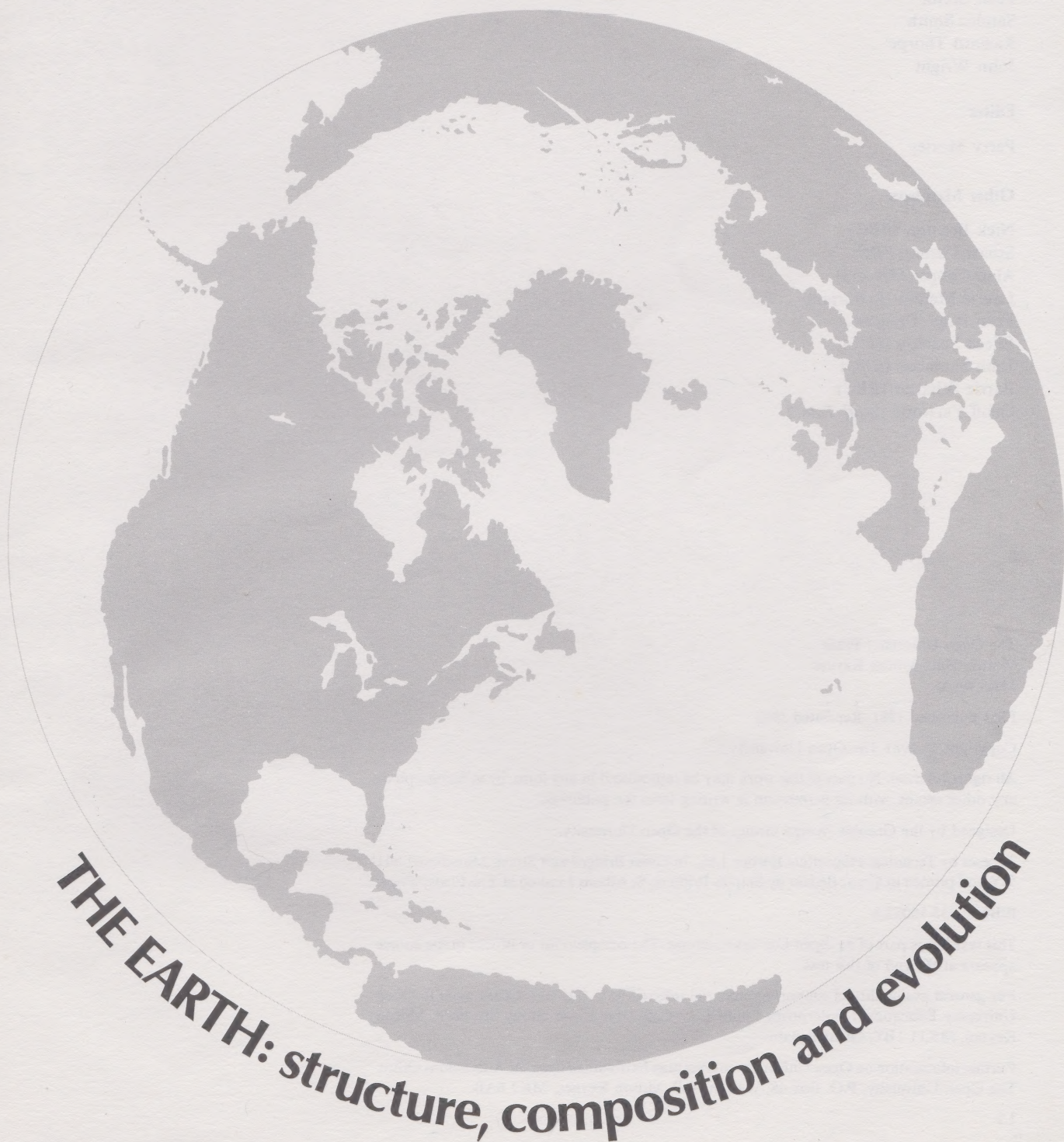THE EARTH: structure, composition and evolution

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phase relations and geochemistry

THE EARTH: structure, composition and evolution

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TABLE A
List of scientific terms and concepts used in this Block

Introduced in the Science Foundation Course or earlier in this Course	S100* Unit No.	S101** Unit No.	S237 Block No.
alkali feldspars			1
aluminosilicate minerals			1
andesite	26, UTE†	27	1
basic rocks			1
β-particle	6, 31	31	
chain silicates			1
chemical equilibrium	9	14	1
chondrites			1
convection	25	6/7	2
coupled substitution			1
cumulates			2
diorite			1
eclogite			1, 2
endothermic reactions	11	15	1
enthalpy	11	15	1
exponential decay	2	26	
exothermic reactions	11	15	1
fayalite			1
forsterite			1
fractional crystallization	UTE	27	1, 2
granite	26	4	1
granodiorite			1, 2
half-life	2, UTE	10/11, 26	
ionic charge			1
ionic radius (size)			1
island arc	24	6/7	
isomorphism			1
isotopes	6	10/11	
magma	24	4	1
magma chamber			2
major elements			1
mass spectrometry	6	10/11	1
minor elements			1
modal analysis			1
neutron activation analysis			1
olivines			1, 2
partial melting	UTE	27	1, 2
peridotite	22	4	1, 2
phenocrysts			1
plagioclase feldspars			1
principle of uniformitarianism	26	26	
pyroxene			1
quartz			1
radioactive decay	6, 31	31	1
refractive index	28	9	
solid-solution series			1
spinel			2
stability fields			1
straight-line graph	HED	HED, MAFS	
trace elements			1
uranium–lead dating	UTE	26	
valency	8	12	
volume of reaction			2
X-ray fluorescence spectrometry			1

Study guide

Block 1 introduced you to the origin of the chemical elements and their distribution in minerals and rocks. Block 2 jumped to the much larger framework of the planet itself and showed how, from largely geophysical evidence, it has been possible to build up a picture of its internal structure. For the most part that structure reflects variations in chemical composition, and in Block 3 we turn now to the processes that determined those chemical variations. For chemical differences to be developed, material must be able to move about and this is obviously easier in liquids than in solids. In this context the liquids are molten rock, and hence the processes that govern the movement of material within the Earth are *igneous processes*.

Igneous processes are those that involve reactions between solid minerals and magmatic liquids—both when a rock is melting and later when the liquid (or melt) cools and crystals form.

In Section 1 you are reminded about those processes of *partial melting*[A]* and *fractional crystallization*[A], which you have already met.

Section 2 then begins an introduction to one of the major topics of this Block—*phase diagrams*. Phase diagrams are simply a graphic way of illustrating what phases (for example, minerals and liquids) are going to exist under particular physical conditions. Although they often look daunting at first, they are really quite easy to use and it is most important that you become familiar with them since they are used widely in many branches of the Earth sciences.

Somewhat more complex phase relations are discussed in Sections 3 and 4, and in TV 06 and AV 05, but throughout the text phase diagrams are handled qualitatively.

When some of us first learnt to use phase diagrams we found that our understanding was helped considerably by doing very simple calculations using what is known as the *phase rule*. Therefore, a brief introduction to the phase rule is included in Appendix 1, together with some worked examples. We stress that it is just another way of handling the material discussed in Sections 2–4 of the text, but urge you to devote some time to using it since your reward will be a fuller understanding of phase relations.

Section 5 explores how the crystallization of different minerals from a magma changes the composition of the liquid, illustrating the arguments on *chemical variation diagrams*. In the later part of Section 5 and in Section 6, these are combined with phase diagrams in a preliminary discussion of the processes leading to the formation of continental crust. Section 7 introduces the slightly different techniques used to evaluate the behaviour of *trace elements*[A] in igneous processes; while Section 8 focuses on isotopes of the element *strontium* and shows how, since one of them is produced by long-lived radioactive decay, they may be used both to *date* rocks and minerals and to study how the composition of segments of, for example, the Earth have *evolved* through time.

In summary, the four major topics of this Block are phase relations (and the use of phase diagrams), major-element variations (chemical variation diagrams), trace elements, and isotopes. With that in mind we estimate the study time for different Sections in terms of Course-Unit equivalents to be:

Sections 2–4	1.0 CUE
Sections 5–6	0.4 CUE
Sections 7–8	0.6 CUE

These estimates include an allowance for studying TV 06 and AV 05 (and their Broadcast Notes) in Sections 2–4, and TV 07 and AV 06 in Sections 7 and 8.

As in previous Blocks, particularly important concepts and summaries are highlighted by the use of red rules in the text and there are also summaries of a more general nature at the end of each major text Section. Following each summary you will find that the Objectives for the appropriate Section are given, together with some SAQs. To help you revise the Block, all the Objectives are collected together at the

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*In this Block we have indicated terms and concepts that are re-used from the Science Foundation Course or from previous Blocks of this Course by a superscript A. You will find a list of these terms and concepts, with the appropriate references, in Table A.

end of the Block where they are cross-referenced to the relevant SAQs and ITQs. It is particularly important to read the answers to the ITQs, as these often contain steps in the arguments being developed in the associated text. There are some references in this Block and in AV 06 to *Colour Plates 1–48*.*

1 Introduction

Volcanoes are the most spectacular evidence that igneous processes are active at the present time (Figure 1). Liquid lava forms lakes of molten rock, which sometimes overflow and devastate the surrounding countryside. Lumps of solid rock (known as volcanic 'bombs') are hurled high into the air and most volcanoes give out large quantities of ash and gas. All these materials clearly come from deep in the Earth— they are the more obvious products of igneous processes.

FIGURE 1 An active volcano on the volcanic island of San Benedicto in the Pacific Ocean about 350 miles off the coast of Mexico.

In the Science Foundation Course it was emphasized that igneous processes are mainly responsible for the chemical variations that exist in the Earth. The principles which govern such processes are the same now as they have always been (the *principle of uniformitarianism*^A holds), so by studying present-day examples we may come to understand the chemical and thus, perhaps, the physical evolution of our planet.

Figure 2 is a sketch section of what may occur beneath a volcano. Somewhere at depth there must be a zone of melting—the geological environments and the mechanisms by which this may occur are discussed in Block 4. The liquid (usually referred to as the melt, or *magma*^A) is less dense than the solid rock and once a reasonable amount has formed (perhaps more than 5–10 per cent of the original rock), it will tend to rise towards the Earth's surface. As it rises, it will cool and crystals will form (as you have seen in AV 02). If these early crystals are denser than the liquid they will tend to sink; if not, they will be carried upwards and still be present in the liquid when it is erupted. Depending on the structure of the individual volcano, this early crystallization may occur as the liquid passes up through the conduits, or in near-surface *magma chambers*^A where magma sometimes collects before eruption.

The *texture* of an igneous rock provides clues as to when, or more particularly at what depth, its crystals may have formed. This is illustrated by the photomicrographs of two different volcanic rocks in Figure 3. If crystallization takes place under conditions of slow cooling at depth, there is sufficient time for relatively large crystals (with good crystal form) to grow. Alternatively, a liquid that is erupted on the surface and therefore cools very rapidly will form either very tiny crystals or perhaps even volcanic glass. (Glass is formed when cooling occurs so quickly that there is no time for any crystals to grow.) Figure 3a is a very fine-grained basalt which we may infer crystallized rapidly on the surface. Figure 3b
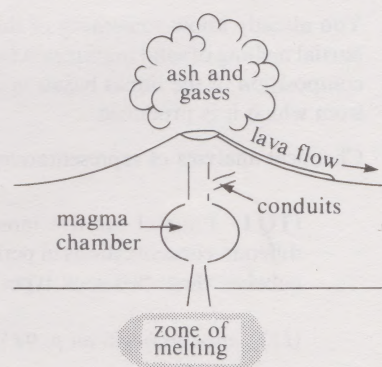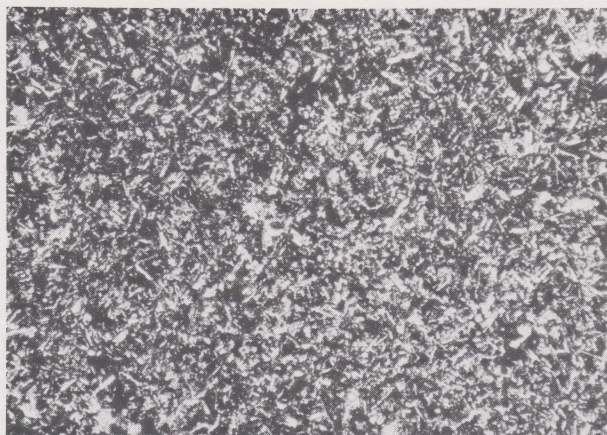

FIGURE 2 Sketch section through the crust and upper mantle beneath a volcano.

*The Open University (1981) S237 *Colour-plate Booklets*, The Open University Press.

(a)
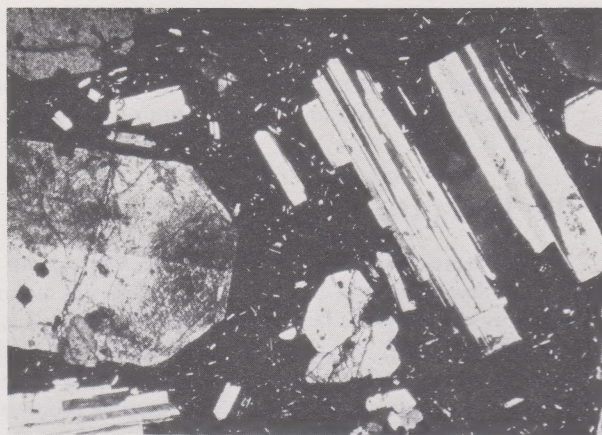
(b)

illustrates a basalt that has some large crystals (called *phenocrysts*[A]) set in a groundmass of much smaller crystals; we would conclude that the phenocrysts crystallized at depth *before* the groundmass minerals crystallized on the surface.

Thus the texture of an igneous rock can give us some idea whether individual minerals crystallized at depth or on the surface, and that in turn tells us the *order* in which the different minerals have crystallized. This, as we shall see later, is extremely important when it comes to unravelling the history of igneous rocks. Two widely used concepts in relation to igneous processes are *partial melting*[A] and *fractional crystallization*[A]. In our discussion of the volcano in Figure 2, we suggested that the liquid may leave the 'zone of melting' once more than 5–10 per cent of the original rock was molten. Since it is most unlikely that complete melting would occur, most igneous liquids reflect only *partial* melting of their source rock. Fractional crystallization, by contrast, may take place as the liquid cools and crystals form, either in the magma chamber and/or in conduits *en route* to the surface. Thus a volcano may be regarded as the surface expression of a vast natural laboratory in which a variety of igneous processes are taking place. Later in this Block we shall attempt to understand those processes by studying the chemical compositions of the minerals and rocks collected on the surface and by trying to reproduce them with experiments in our own laboratories.

Let us start by helping you to recall what is meant by partial melting and fractional crystallization. This Section is designed to establish the background to the more detailed treatments that follow, so you should read it carefully. Don't worry if you don't understand it fully at first; it will all become much clearer later on.

Partial melting

You already know something of the production of basalt magma (i.e. liquid) by partial melting of solid mantle *peridotite*[A]. The most important point here is that the composition of the liquid basalt is very different from that of the solid peridotite from which it is produced.

Chemical analyses of representatives of both rock types are shown in Table 1.

ITQ 1 Four of the five most abundant constituents of basalt have very different concentrations in peridotite. In what way do these abundances differ between these two rock types?

(*ITQ answers begin on p. 94.*)

But *why* does this happen? Why is it that, when you heat up peridotite until it begins to melt, you get something so different in composition?

The short answer is very simple: when you melt a pure substance, like ice or lead or paraffin wax, it melts at a single characteristic temperature (its *melting point*) and the liquid has the same composition as the solid you started with. However, if you take two or more solid substances which each have different melting points, mix them together and then heat the mixture, it should come as no surprise that the mixture will *not* all melt at a single temperature. The substances with lower melting points will tend to melt at lower temperatures than those with higher melting points and thus the whole mixture will melt over a *range of temperatures*.

FIGURE 3 Photomicrographs of two volcanic rocks.
(a) Very fine-grained 'glassy' basalt (magnification × 10).
(b) Basalt with large phenocrysts set in a fine-grained groundmass (magnification × 10).

The following terms are defined in *Colour Plates 35–48* (see Plates 35–39):
crossed polars
interference colours
relief
texture

TABLE 1 Chemical analyses of typical peridotite and basalt (weight per cent)

	Peridotite	Basalt
SiO_2	45.6	46.9
TiO_2	0.20	2.0
Al_2O_3	2.6	13.1
Fe_2O_3	1.9	1.0
FeO	5.9	10.
MnO	0.13	0.15
MgO	41.4	14.6
CaO	1.9	10.2
Na_2O	0.19	1.7
K_2O	0.12	0.08
P_2O_5	0.03	0.21

Similarly, the *chemical composition* of the first liquids to form (that is, those at lower temperatures) will be dominated by the *composition* of the substances with the lower melting points. Thus the basalt and the peridotite in Table 1 have different chemical compositions because basalt consists predominantly of those minerals in peridotite that have the lower melting points. We may begin to think of igneous rocks being made up of high- and low-temperature minerals. The latter will melt first when you heat up the rock, while the former may never melt completely and will therefore tend to be left behind when the liquid is removed. In between, there are minerals that have intermediate melting points.

> **ITQ 2** The mineral *olivine*[A] can have a range of chemical compositions: you were introduced to its general composition in Block 1 (Table 9), but Table 2 gives a more detailed analysis of a typical olivine (oxides in weight per cent).

TABLE 2

SiO_2	TiO_2	Al_2O_3	FeO and Fe_2O_3	MnO	MgO	CaO	Na_2O
40.8	0.1	0.04	11.1	0.08	46.9	0.04	0.05

Note K_2O and P_2O_5 contents are negligible.

Compare this analysis with those for the basalt and peridotite in Table 1:

(a)   Which of those rock types is likely to contain more olivine?

(b)   Does that suggest that olivine is a high- or a low-temperature mineral?

The terms high- and low-temperature must be used merely as relative terms when describing the melting behaviour of minerals. This is because one of the really surprising consequences of heating a mixture of different substances is that the mixture *starts* to melt at a temperature that is *lower than the melting points of any of its constituents*. Thus we mix salt with the water on our roads to stop it freezing. The melting point of pure salt is 800 °C and that of water is 0 °C and yet, if we mix them in the correct proportions, the mixture will remain liquid at even −20 °C. Common solder is a 1:1 mixture of tin and lead and it starts to melt at about 115 °C; yet pure tin melts at 132 °C and pure lead at 327 °C. It is the same with rocks. For instance, you may recall from Block 1, two important constituents of *granite*[A] are *quartz* (SiO_2)[A] and *alkali feldspar* $(KAlSi_3O_8)$[A]. The melting points of these minerals *by themselves* are respectively about 1 713 °C and 1 530 °C. Yet the melting temperature of granite can be as low as 650 °C.

We shall return to this topic in greater detail later on, but now let us look at the other important principles governing igneous processes.

Fractional crystallization

In some respects we may regard crystallization as the reverse of melting. We are dealing with the cooling of liquids so that they freeze (crystallize) and solidify, rather than with the heating of solids so that they melt.

If you consider a pure substance like water, it freezes at a particular temperature (its *freezing point*, which is naturally the same temperature as its melting point) and the composition of the ice is the same as that of liquid water (H_2O). So freezing of ice does not change the composition of H_2O. And it is the same with molten lead, or paraffin wax, or any other pure substance.

However, if we cool a liquid which is a mixture of different substances, each with its own individual freezing temperature, then it will solidify over a *range of temperatures*. The high-temperature substances (those with the highest freezing temperatures) crystallize first. Because their composition is different from that of the other substances in the original mixture the composition of the remaining liquid must change. This point is well illustrated by the crystallization of olivine from basalt magma. We have already argued that olivine is a high-temperature mineral (ITQ 2) so we would expect it to be one of the first minerals to crystallize as we cool a basaltic (or *basic*[A]) liquid.

> Consider the chemical compositions of olivine in ITQ 2 and the basalt in Table 1. What would happen to the composition of the basalt liquid if olivine were able to crystallize from it?

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The basalt liquid will become *depleted* in the element that is more abundant in olivine than in the liquid (MgO). It will become *enriched* in those elements that are much less abundant in olivine than in the liquid (for example, TiO_2, Al_2O_3, CaO and Na_2O).

So far this discussion has been all about *crystallization*, but where does the fractional aspect come in?

Look at Figure 4. The boxes represent two samples of basaltic liquid. In sample (a), the basalt liquid cools and olivine crystallizes, which changes the composition of the liquid. However, because the olivine is still within our sample 'box', *the composition of our total sample hasn't changed*. Initially, exactly the same thing happens in sample (b): olivine crystallizes and this changes the composition of the liquid. But, this time, the olivine sinks out of the 'box' and is therefore separated physically from the liquid. In this case our original sample of basaltic liquid has been subdivided into two *fractions*: (i) olivine crystals, and (ii) liquid which no longer has the same composition as the original liquid. Thus sample (b) (that is, its 'box') has had its composition changed by *fractional crystallization* of olivine.
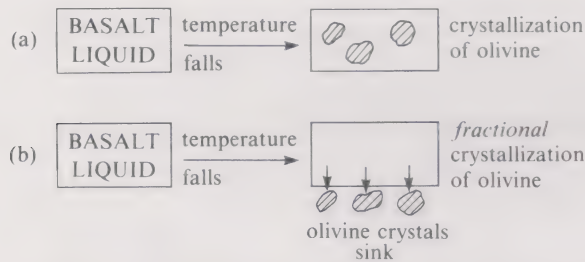
FIGURE 4 A schematic sketch illustrating the difference between (a) crystallization of olivine and (b) fractional crystallization of olivine.

The important points about fractional crystallization are therefore that (i) the crystals have a different composition from the liquid, and (ii) the *initial sample is physically sub-divided into separate fractions*—crystals and liquid.

So, in summary:

1   A complex mixture of solids (which is what most rocks are) generally melts over a *range* of temperatures. The minerals with the lowest melting points tend to melt first so the composition of the liquid produced when melting begins is dominated by the composition of the low-temperature minerals. Thus a 'partial melt' generally has a very different composition from that of the original source rock.

2   When a liquid made up of a mixture of chemical substances (which is what all igneous magmas are) cools and solidifies, crystallization (freezing) takes place over a *range* of temperatures. High-temperature minerals crystallize first (that is, at the higher temperatures) and most of the crystallizing minerals have compositions very different from that of the original liquid. *Fractional crystallization* takes place when the crystals and liquid become physically separated from one another.

We have deliberately spent a long time on this extended revision, because it leads us into the central topic of the first part of this Block—phase diagrams. If it has not occurred to you to do so before, you could now ask yourself how is it that we can discuss melting and crystallization relationships in salt–water mixtures, peridotite, granite and so on.

The occurrence of phenocrysts in igneous rocks (Figure 3b) provides qualitative evidence that magmas crystallize over a range of temperatures. However, these relationships can only be properly studied by laboratory experiments. Mixtures of various substances are subjected to a range of temperatures (and pressures) in the laboratory, and the compositions of the products are then analysed. By far the most convenient way of depicting and describing those results, whether we are talking about salt–water mixtures, metal alloys, or rocks, is by the use of phase diagrams, which are really little more than a special kind of graph.

2 Some simple phase diagrams

Study comment The next three Sections serve to introduce phase diagrams — how they are constructed and in particular how they are used to describe and evaluate relations between co-existing crystals and liquids. Variations in both two and three dimensions are discussed, but the principles are the same throughout and it is most important that you understand and feel confident about using the simpler diagrams in Sections 2 and 3 before tackling phase relations portrayed in three-dimensional models and block diagrams (Section 4.3). TV 06 and AV 05 are very closely linked to Sections 3 and 4.

As the formal definitions of the terms *phase* and *phase diagram* are rather esoteric, the simplest way to introduce you to them is to show you some simple examples of the construction, use and application of phase diagrams. The definitions will then be much easier to comprehend.

Phase diagrams generally illustrate the conditions of *temperature*, *pressure* and *composition* under which different phases exist. However, variations in three directions are difficult both to draw and to envisage and it is therefore much simpler to keep one of the three variables constant and to show what happens as the other two vary. Thus the phase diagrams which you will meet most often plot either pressure against temperature, or temperature against composition.

2.1 Phase diagram for H$_2$O—ice, water and vapour

Water, or more precisely H$_2$O, is a substance which we all know can exist as a solid (ice), a liquid (water) and a vapour under the conditions available to us in our own kitchens. We are also aware that ice melts at 0 °C and water boils and changes to steam at 100 °C, but these temperatures are what we observe at the atmospheric pressure (10^5 N m^{-2} or 1 atm) under which most of us live.

> What happens when we change the pressure? Would water still boil at 100 °C either in our pressure cookers or in the rarefied air in mountainous areas such as the Andes or the Himalayas?

To answer such questions, we can do a series of very simple experiments. We can subject samples of water to different temperatures and pressures, observe whether they exist as ice, liquid water or water vapour and plot the results on a diagram of pressure against temperature. There are no changes in our third variable, composition, because ice, water and water vapour are all H$_2$O.

The results from a series of experiments are plotted on Figure 5a, where each point represents an individual experiment and records whether H$_2$O was present as solid (ice), liquid or vapour at that particular temperature and pressure. You can see that the symbols for solid, liquid and vapour all cluster together in different 'areas' on the diagram and thus we can draw in lines marking out the boundaries between those areas that share the same symbols.

For clarity these lines have been reproduced in Figure 5b — they delimit areas on the diagram that represent the conditions of pressure and temperature under which H$_2$O exists as a solid, a liquid or a vapour. To put it another way, they are areas in which H$_2$O is *stable* as ice, liquid water, or water vapour, and they are therefore referred to as the *stability fields*$^\triangle$ of these three substances.
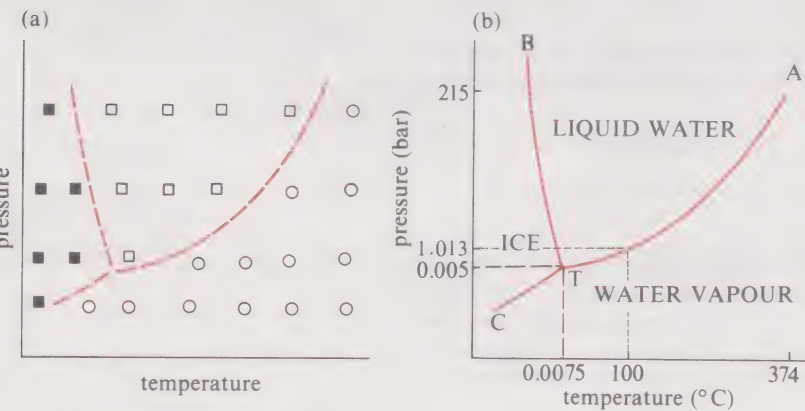

FIGURE 5 Diagrams of pressure against temperature for the system H$_2$O.
(a) The results of experiments to determine the stability fields of ice (filled squares), liquid water (open squares) and water vapour (open circles).
(b) Phase diagram for the system H$_2$O illustrating the stability fields of ice, liquid water and water vapour. Note the logarithmic scale on the vertical axis.

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Instead of the rather vague word 'substance' we may now use the more precise term *phase*. A *phase* is defined as something that differs chemically and/or physically from the rest of the system that is being considered. Thus, in Figure 5, ice, liquid water and water vapour are all different phases—they share the same composition (H_2O), but differ in their physical state. As we shall see later, different phases can also have the same physical state but different compositions: for example, two minerals in a rock. Rarely, different solid phases even have the same composition (as in the *aluminosilicate minerals*[A], Al_2SiO_5, which were introduced in Block 1, Figure 49).

Returning to Figure 5, we may now refer to it as a *phase diagram*: in formal language it illustrates the *stability fields* of three different *phases* (ice, liquid water and water vapour) in the *system* H_2O. The solid lines mark the boundaries of the stability fields of the three phases and are therefore called *phase boundaries*.

Note   The term *system* is simply defined as any part of the universe *we* wish to isolate; the choice is ours and it should reflect the problem we wish to discuss. Figure 5 illustrates the system H_2O at different temperatures and pressures, while elsewhere in the Course we shall consider systems ranging from one or two minerals to the whole planet Earth.

The results in Figure 5 indicate which phase is stable under particular conditions of pressure and temperature. However, they tell us nothing about what happens if for example we increase the temperature on a sample and move it *across* a phase boundary. Boiling a kettle until all the water has been converted to steam is to move across the phase boundary between liquid water and vapour; the important points are (i) it takes quite a long time, and (ii) although heat is still being supplied by the stove, the temperature remains at about 100 °C until all the water has been boiled off. The temperature of your tea is the same whether the kettle has been boiling for five or thirty-five minutes!

> What is happening to that heat which is being added to the kettle while it is boiling? After all, it doesn't raise the temperature of the boiling water.

The short answer is that a certain amount of *extra* heat is required to convert H_2O from liquid water to vapour with no change of temperature, that is, the reaction

$$H_2O_{liquid} \longrightarrow H_2O_{vapour} \qquad (1)$$
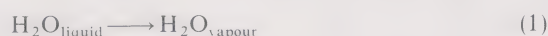
is *endothermic*[A]—its *enthalpy*[A] of reaction (ΔH) is positive (Block 1, Figure 43). (Molecules of H_2O are bound more closely together in a liquid than in a vapour, and extra energy has to be introduced to overcome the forces, or 'bonds', that exist between the molecules of H_2O in the liquid.) It follows that the reverse reaction, vapour $\longrightarrow$ liquid is *exothermic*[A]—it gives out heat. This heat, which is, if you like, *hidden* in the vapour and released when the vapour is converted to a liquid, is termed *latent heat*. It is the reason that burns caused by steam are so much worse than those caused by hot water.

Conversely, latent heat is the amount of heat that must be added to a liquid to convert it to a vapour. In general, all phase changes between solid, liquid, and vapour involve latent heat. It must be added to those reactions that go towards a higher-energy state, namely solid $\longrightarrow$ liquid, solid $\longrightarrow$ vapour, liquid $\longrightarrow$ vapour, and it is released by reactions that proceed in the reverse direction.

> **ITQ 3**   A sample of ice was heated continuously and the temperature was recorded every two minutes. The results are presented on a graph of temperature against time (Figure 6).
>
> (a)   Mark the boiling point and the melting point on the temperature axis.
> (b)   Label those portions of the graph where H_2O existed as ice, liquid water and water vapour.
> (c)   For how long was H_2O present as liquid water *only*?
> (d)   For how long did this system contain *any* liquid water?

The sample in Figure 6 was moved from the stability field of ice, through that of liquid water and into the stability field of water vapour. The *phase boundaries* it passed through marked the conditions under which one phase converted to another. *At* a phase boundary, the two phases on either side of it exist together. Moreover, *on such a phase diagram, a phase boundary represents the only conditions under which two phases can exist together.*

Look at Figure 5b and fill in the letters in the spaces below:

Line ... represents the boiling point curve (i.e. liquid ⇌ vapour).

Line ... represents the melting point curve (i.e. solid ⇌ liquid).

Line ... represents the *sublimation point* curve (i.e. solid ⇌ vapour).

sublimation point

The order should be A, B, C.

In Block 1 you met some simple thermodynamic facts relating to the changes in *enthalpy* (ΔH) and *volume of reaction*[A] (ΔV) that occur as reactions proceed. If ΔH and ΔV have the same sign, then the slope of the boundary (at which the reaction takes place) on a graph of pressure against temperature is positive: if ΔH and ΔV have opposite signs the slope is negative (Block 1, Figure 45).

> Consider the boiling-point curve (A) on Figure 5b; is its slope positive or negative?

> From what you know of their relative densities, is ΔV for the reaction liquid water $\longrightarrow$ water vapour positive or negative?

Since water vapour is much less dense than liquid water, ΔV for the reaction liquid water $\longrightarrow$ water vapour is positive. Moreover, because the slope of the boiling-point curve for H_2O (line A, Figure 5b) is positive ΔH and ΔV must have the same sign. So ΔH is also positive and the reaction is *endothermic*. We have explained in thermodynamic terms why our kettle of water needs a certain amount of extra heat (ΔH) before the water in it at 100 °C converts to steam.

> **ITQ 4** Using similar arguments to those outlined above for the reaction liquid water $\longrightarrow$ water vapour, deduce whether the reaction liquid water $\longrightarrow$ ice is exothermic or endothermic.

We are now in a position to answer some of our initial queries about the properties of water. The positive slope of line A in Figure 5b provides the basis for the use of the pressure cooker. At higher pressures, water will boil at a higher temperature, so, by cooking at a higher pressure than usual in a pressure cooker, a higher temperature can be reached, thereby decreasing the time taken to cook a meal. The opposite effect is observed by mountaineers, who find that water boils at lower temperatures on the tops of mountains where air pressure is lower and tea can be no more than luke-warm!

The negative slope of line B reflects the fact that ice is less dense than water (see ITQ 4); the freezing point of water decreases with increasing pressure. A practical application of this lies in the use of ice skates. Under the pressure of a skate blade, the ice melts to form a thin film of water, which lubricates the blade, enabling skaters to move smoothly.

The point T in Figure 5b is the only point at which three phases—solid, liquid and vapour—are in equilibrium, that is, they can exist stably together. This is known as the *triple point* and occurs at 0.0075 °C and 0.005 bar for pure water. Note that this does not correspond to the freezing point of ice in your refrigerator, which is at 0 °C and 1 atm pressure. For the purpose of making a temperature scale, the freezing point of ice was defined as 0 °C at 1 standard atmosphere (1.013 bar).

triple point

Three phases cannot co-exist stably under any conditions other than those at the triple point. Under conditions lying precisely upon lines A, B and C, two phases can co-exist stably, but under any other conditions only a single phase can exist stably.

You have already met an example of a triple point in a silicate system in Block 1. Can you remember what it was?

Don't worry if you couldn't recall it, but look at Block 1, Figure 49, which shows the aluminosilicate mineral phase diagram. It contains a triple point where all three minerals may exist together in nature.

Study comment In addition to the general way phase diagrams are discussed in this text, phase relations may also be described using a very slightly more arithmetic technique—the *phase rule*. This is an extremely simple equation, derived by J. Willard Gibbs in the 1870s, relating the number of phases and components in a system which are present at equilibrium. Many people find the phase rule an extremely useful additional technique for understanding and finding their way around phase diagrams, and it is therefore included in Appendix 1. We emphasize that it is essentially another, albeit more elegant, way of reiterating what is discussed in the text, but it is important that you become familiar with the phase rule because you will find it of considerable help when dealing with more complex phase diagrams in this and other courses. At this point you should therefore tackle part (i) of Appendix 1.

phase rule

2.2 Construction of simple phase diagrams for rocks and minerals

H_2O exists as solid, liquid and gas at conditions close to those under which we live and it is therefore relatively easy to design experiments to look at the relationships between the different phases (Figure 5). By contrast, many rocks do not start to melt until temperatures of 700–800 °C are reached and then they may not be completely molten until 1 200–1 300 °C. In addition, they do not melt at the Earth's surface, but rather in the uppermost mantle and/or in the deeper portions of the crust. These regions correspond to pressures of approximately 10–40 kbar; thus, to study the behaviour of different minerals during melting (and crystallization), our experimental technique must be able to handle high temperatures and pressures.
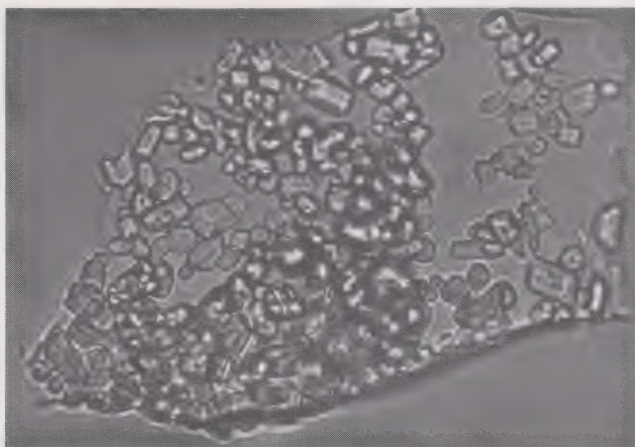
FIGURE 7 Photomicrograph illustrating quenched crystals and glass after an experimental 'run' (magnification ×90).

In practice, most of the experimental results that we shall be looking at were obtained using a *quenching method*. Several metallic capsules containing samples of the same composition are prepared and then subjected to a variety of temperatures and pressures. Each sample is held at a particular temperature and pressure until *chemical equilibrium*[A] has been achieved, that is, when the mixture of phases appropriate to that pressure and temperature have been produced—this may take several hours or even weeks. Then it is cooled extremely fast (that is, quenched) so that there is no time for the phases to interact while the sample is cooling. Material that was liquid under the conditions of equilibrium should form a clear glass at room temperature, while any minerals present should cool without changing their composition (Figure 7 and *CB**, Plate 44).

quenching method

* The Open University (1981) S237 *Colour-plate Booklets*, The Open University Press.

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Figure 8 presents the results of a series of hypothetical experimental runs on a single mineral. A number of points are worth noting:

1   As in Figure 5a, each point on the diagram represents one experimental run.

2   Once the experimenter has a rough idea where the phase boundary is located, it is only necessary to subject further samples to conditions that are close to it.

3   The *accuracy* with which the phase boundary is known depends both on the number of the experimental runs and the spacing between them in Figure 8. If the points in Figure 8 were more widely spaced then there would obviously be much less constraint on where the boundary was drawn.

4   *Equilibrium* must exist in the sample capsule before quenching or the whole experiment is worthless. You should already know something about the concept of chemical equilibrium as a state of dynamic balance. In experiments, samples are considered to have reached equilibrium when no more changes (for example, solid ⟶ liquid, or one mineral to another) can be seen to take place, no matter how much longer they are left under the particular conditions of pressure and temperature.

The vast majority of rocks consist of more than one mineral. Moreover, the different minerals may be expected to melt at different temperatures. Thus the melting behaviour of a rock is more complex. In particular, as discussed in Section 1, we can expect it to melt over a wide range of temperatures. This situation is depicted in Figure 9, where the results of a series of hypothetical experimental runs on a rock are presented on a diagram of pressure against temperature.

As in the case of the single mineral (Figure 8) there is an area (that is, a field) where only solid material is observed and a field where no crystals are seen and everything has melted. However, in contrast to Figure 8, there is also a wide field (between the lines A and B) where both liquids and solids co-exist.

What do the lines A and B represent?

Line A is the *solidus*, which marks the boundary between the field where some liquid is present and that where the material is entirely solid. The solidus is more formally defined as *the curve, or curves, below which the system is entirely solid*. It depends not only on the pressure and temperature (as in Figures 5, 8 and 9), but, as you will see later, it may also depend on the composition of the system.

Line B is the *liquidus*, which is defined as *the curve, or curves, above which the system is completely liquid*. It also must depend on pressure, temperature and composition.

These definitions of liquidus and solidus apply to all the phase diagrams we shall be looking at. In two-dimensional diagrams (for example, Figure 9), the liquidus and solidus are curves or lines, while on the three-dimensional models or diagrams we shall be discussing later, they are surfaces.

So far in this Section on simple phase diagrams, we have concentrated on phase changes that involve a change in physical state *without* any change in chemical composition. Thus the composition of the liquid is the same as that of the solid and both inevitably have the same composition as the system as a whole. This is seen in Figure 5 (H_2O) and we may assume that it was true for the single mineral in Figure 8. However, rocks are made up of many minerals and that has two important consequences relevant to this discussion.

(i)   Rocks melt, not at a single melting point, but over a *range* of temperatures.

(ii)   The liquid produced on *partial* melting does *not* have the same composition as that of the original rock.

Similarly, igneous rocks crystallize over a range of temperatures, and the first minerals to form do *not* have the same composition as the melt.

Thus, although Figure 9 is correct, it is concealing a vast amount of important information. The composition of the solid (crystals) in the field between A and B is different from that in the solid-only field, while the composition of the liquid (glass) in the field between A and B is not the same as that in the liquid-only field.

Experimental work need not be restricted to observing merely the physical state of the material. It is much more exciting that we can analyse the crystals and the glass (that is, the liquid) in our quenched samples and explore how the compositions of the crystals and the liquid vary. In Section 3 we shall therefore introduce some
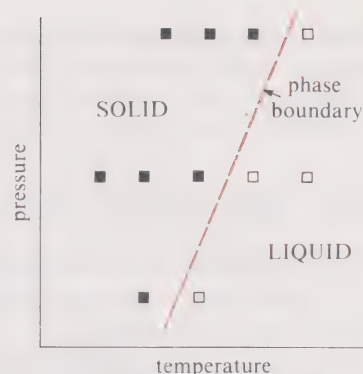
FIGURE 8   Construction of a phase diagram of pressure against temperature for a single mineral. Black squares represent samples consisting only of solid material; open squares represent samples consisting of glass (that is, quenched liquid).

solidus

liquidus
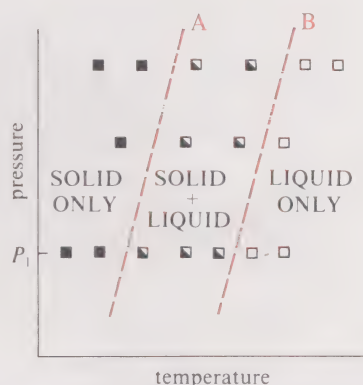
FIGURE 9   Construction of a phase diagram for a rock that melts over a range of pressure and temperature. The symbols are the same as in Figure 8 except that half-open squares represent samples consisting of both solid material (crystals) and glass (quenched liquid). The lines A and B are discussed in the text.

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simple phase diagrams in which the pressure is held constant and composition is plotted against temperature. In Figure 9 that might be analogous to holding the pressure at P_1 and recording changes in composition as the temperature is increased or reduced across both the solidus (line A) and the liquidus (line B).

2.3 Objectives for Sections 1 and 2

Now that you have completed Sections 1 and 2, you should be able to:

1 Define in your own words, or recognize valid definitions of, the terms flagged in the margins of this Section.

2 Explain why the composition of a liquid produced by partial melting differs from that of the original rock.

3 Indicate that you understand the difference between crystallization and fractional crystallization, and why the latter tends to change the composition of the bulk sample.

4 Use diagrams of pressure against temperature and temperature against time to describe what happens to selected samples under different conditions of temperature and pressure.

5 Undertake simple calculations using the phase rule; e.g. calculate the number of degrees of freedom that exist for a particular assemblage of phases (Appendix 1).

Apart from Objective 1, to which they all relate, the five ITQs in these Sections test these Objectives as follows: ITQ 1: Objective 2; ITQ 2: Objective 3; ITQ 3: Objective 4; ITQ 4: Objective 4; ITQ 33 (Appendix 1): Objective 5.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 1 (*Objective 1*)   Which *three* of the following statements are correct?

(a) A phase boundary is a line on a phase diagram where just one phase is stable.

(b) A sample that plots *on* the liquidus will contain no crystals—it will be completely liquid.

(c) At temperatures below the solidus you would expect a sample to contain no liquid.

(d) Large crystals in a volcanic rock are an indication that it cooled slowly over part of its history.

(e) Latent heat is released from a sample as it is converted from solid to liquid.

(f) Melting or crystallization of the overwhelming majority of rocks does not occur at a single characteristic temperature, but rather over a range of temperatures.

(*SAQ answers begin on p. 100.*)

SAQ 2 (*Objective 2*)   The basalt in Table 1 (p. 8) is heated until two-thirds of it has melted, whereupon the only crystals still present are of olivine. If those residual crystals have the same composition as the olivine in ITQ 2, will the concentrations of oxides (i)–(v) be (a) higher in the melt than in the original basalt? (b) lower in the melt than in the original basalt? (c) similar in both?

(i) SiO_2

(ii) Al_2O_3

(iii)   Total iron (FeO and Fe_2O_3)

(iv)   MgO

(v) K_2O

SAQ 3 (*Objective 4*)   Figure 10 presents the results of a series of experiments to determine the stability fields of vapour, liquid, and solid in the system carbon. Sketch in the phase boundaries and label the melting-point and the boiling-point curves. Is there a *triple point*? If so what is its approximate temperature and pressure?

**SAQ 4** (*Objective 5*)   Negative values of F (degrees of freedom) indicate that it is impossible for the proposed assemblage of phases to co-exist in equilibrium. Can four phases co-exist in equilibrium in a one-component system? (Use the phase rule.)

■ solid   □ liquid   ○ vapour
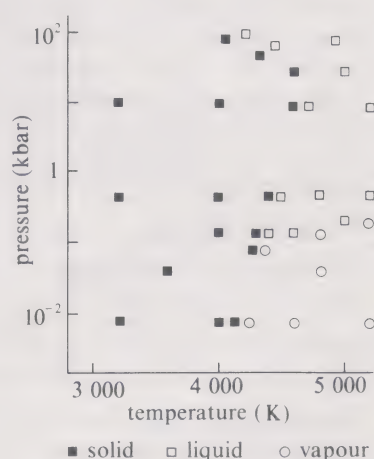
FIGURE 10   A phase diagram of pressure against temperature, illustrating the results of a series of experiments to determine the stability fields of vapour, liquid, and solid carbon. Note that the temperature is in degrees Kelvin (K). For use with SAQ 3.

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3 Compositional phase diagrams for simple eutectic* systems

The discussion of mineral chemistry in Block 1 (Section 3.2.2) pointed out that many *isomorphous*[A] substances tend to form *solid solutions*[A] in which related elements substitute for one another. This results in a range of mineral chemistry within the same mineral family. In this Section we shall start by looking at substances between which solid solution is negligible and then move on to phase diagrams for mineral families such as the *olivines*[A] and *plagioclase feldspars*[A] which are inter-related by solid solution.

3.1 Construction of a simple compositional phase diagram

G and H are two minerals *between which there is no solid solution*. We wish to investigate their phase relations, using the quenching method described earlier, but this time the experimental results are presented on a diagram of temperature against composition. Figure 11 is such a diagram. Conventionally the vertical axis represents temperature and the horizontal axis represents the full compositional range of mixtures between 100 per cent G and 100 per cent H. We cannot illustrate variations in pressure on Figure 11 and so all our experimental results will have to be obtained under the same pressure conditions.
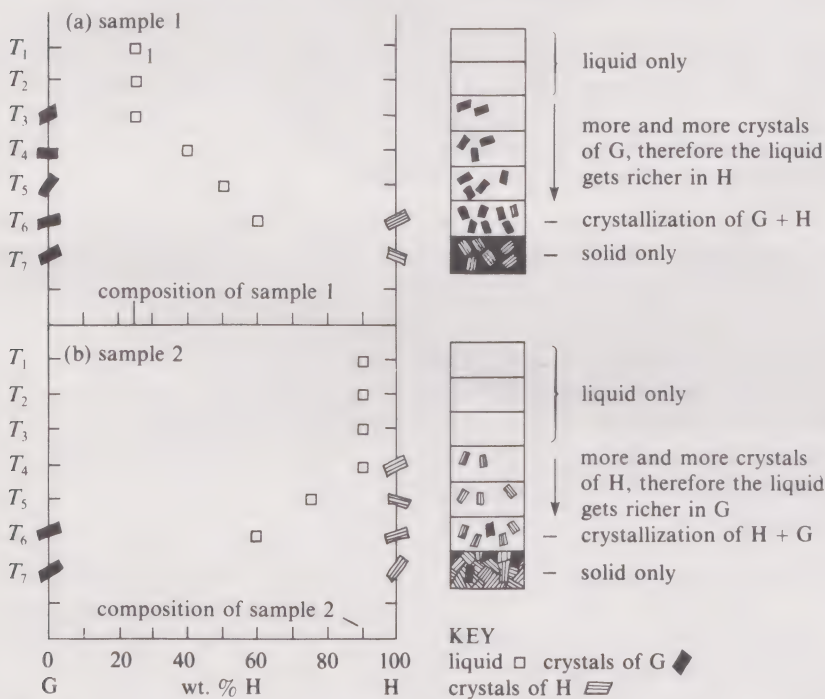
FIGURE 11   Phase diagrams of temperature against composition for samples consisting of mixtures of two minerals G and H.

(a)   Sample 1, 25 per cent H, 75 per cent G.

(b)   Sample 2, 90 per cent H, 10 per cent G.

The sketches on the right illustrate which crystals (if any) are present at each temperature T_1 to T_7.

We shall consider two samples made up of different proportions of G and H, heat them until they are completely liquid and then observe what happens as the temperature is reduced. Sample 1 contains 75 per cent G and 25 per cent H, and at temperature T_1 it plots at point 1 on Figure 11a. As you can see from the sketches to the right of the diagram of temperature against composition, the sample is all liquid at this temperature.

At T_2 the sample is still completely liquid and, since it has only experienced a reduction in temperature, its composition must still be the same as that of the original liquid.

* Don't worry about the word 'eutectic' at this stage; it is defined later in this Section.

On further cooling, the first crystals appear at temperature T_3. Will the composition of these crystals be the same as that of the liquid?

The answer must be a very emphatic *no*. The liquid consists of 75 per cent G and 25 per cent H, but since we have stated that there is no solid solution between G and H, *these first crystals cannot have the same composition as the liquid—they must be either pure G or pure H*. In sample 1, the composition of the original liquid was rich in G and analysis of the crystals shows that they are 100 per cent G. In Figure 11a they therefore plot at the same temperature (T_3) as the liquid, but at the extreme left-hand side of the diagram (that is, at 100 per cent G, 0 per cent H).

As the temperature continues to fall to T_4 and T_5, more and more crystals of G are formed.

What effect will this have on the composition of the liquid? At T_5, for example, does it still consist of 75 per cent G and 25 per cent H?

Again the answer must be *no*. Because only crystals of G are forming, we should predict that the liquid is becoming impoverished in G and therefore relatively enriched in H. This is borne out by the results in Figure 11a; the sample from the lower temperature T_5 contains more crystals of G than those from higher temperatures and therefore the liquid is much richer in H. There is a steady increase in the amount of H in the liquid at lower and lower temperatures. Moreover, given such an increase in the concentration of H in the liquid, it is inevitable that at some stage crystals of H will start to form.

The first few crystals of H appear in sample 1 at temperature T_6—in addition to more crystals of G to add to those which have been formed during cooling from temperature T_3. In Figure 11a, these crystals of H are obviously at the same temperature (T_6) as the liquid and the crystals of G, but they plot on the extreme right-hand side of the temperature–composition diagram (100 per cent H, 0 per cent G).

At the even lower temperature T_7 there is no liquid remaining and the sample is now entirely solid. Can you work out the percentages of H and G in the solid sample?

In spite of the fact that G crystallized before H, we have never actually changed the composition of our *total* sample. Thus the composition of the solid must be the same as that of the original liquid—75 per cent G and 25 per cent H.

Let us now consider the results from sample 2—only this time it is your turn to interpret them! This sample is much richer in H than sample 1, consisting of 90 per cent H and 10 per cent G. The results are presented in Figure 11b and it is most important that you attempt ITQ 5 to make sure that you understand these diagrams of temperature against composition, before tackling the next Section.

ITQ 5   Use the results in Figure 11b to answer the following questions:

(a)   At what temperature (T_1, T_2, etc.) do the first crystals appear?

(b)   What is the composition of those first crystals? Are they (i) 100 per cent G; (ii) 100 per cent H; or (iii) do they have the same composition as the liquid?

(c)   As more and more crystals form at lower temperatures, does the composition of the liquid (i) remain constant; (ii) become richer in G; or (iii) become richer in H?

(d)   What is the lowest temperature (T_1, T_2, etc.) at which some liquid is still present? Is it the same temperature as observed for sample 1 (Figure 11a)?

(e)   What are the percentages of G and H in the entirely solid sample at temperature T_7?

Comparing the results from samples 1 and 2 (Figures 11a and 11b), you should note a couple of points.

1   The pattern of crystallization is very similar for both samples. One is rich in G and crystals of G form over a range of temperature. The other is rich in H and crystals of H form over a range of temperature.

2   The liquid at the lowest temperature (at T_6) has the *same composition* (60 per cent H, 40 per cent G) for both samples—and that in spite of the fact that sample 1 has 25 per cent H and sample 2 has 90 per cent H.

The lowest-temperature liquid of *any* sample that consists of *any* mixture of G and H always has this same composition of 60 per cent H, 40 per cent G, at this pressure. Moreover, for samples in which (like sample 1) crystals of G form before those of H then *once the first crystals have formed* the composition of the liquid will be the same as that of the liquid in sample 1 *at the same temperature*. That is, at T_3 it will be 75 per cent G, 25 per cent H; at T_4 60 per cent G, 40 per cent H; and so on (Figure 11a). Similarly the liquid from samples rich in H will be the same as that from sample 2 at the same temperature (10 per cent G, 90 per cent H at T_4; 25 per cent G, 75 per cent H at T_5; and so on). Thus we may start to construct a general phase diagram for the system G–H by plotting the 'paths' along which the liquids from samples 1 and 2 move *once the first crystals have formed*. This is done in Figure 12a.
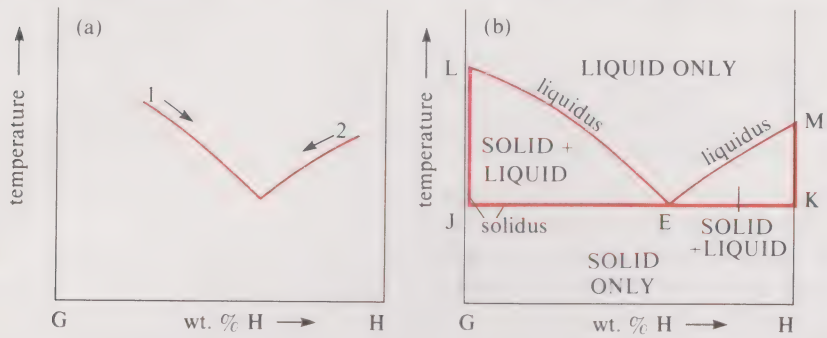
FIGURE 12   Phase diagram of temperature against composition for the system G–H.

(a)   The paths taken by the liquids in samples 1 and 2 on Figure 11 *after the first crystals appeared*.

(b)   Complete phase diagram illustrating the general features of a binary eutectic system. See text for discussion.

By carrying out more cooling experiments with samples that are richer in G than sample 1 and richer in H than sample 2, we may complete these lines representing the compositions of liquids in equilibrium with crystals of either G or H; see Figure 12b. The horizontal line JEK marks the temperature (in this case T_6 in Figure 11) below which all mixtures of H and G are completely solid.

Figure 12b is now a typical example of a phase diagram of temperature against composition for mixtures of two substances between which there is no solid solution. We shall therefore describe its general features and then use it to discuss the phase relations between two such substances. This after all is how phase diagrams are commonly used in geology. We do the experiments to construct them and then use them to interpret the relationships between the minerals (phases) that we recognize in rocks.

3.2   General features of a diagram of temperature against composition for a simple eutectic system

The phase diagram of temperature against composition in Figure 12b contains the same five features as the phase diagram of pressure against temperature in Figure 9: a solid-only field, a liquid-only field, a field where both solid and liquid are present, a solidus and a liquidus.

Let us look at these in turn:

1   *The liquid-only field*   In our earlier experiments (see Figure 11), samples 1 and 2 were completely liquid at high temperatures and, in fact, all samples that plot above (on the high-temperature side) of the curve LEM (Figure 12) are entirely liquid.

If we turn that around and say that 'the liquid-only field is bounded on its low-temperature side by the curve LEM', what would you call the curve LEM and which line does it correspond to on Figure 9?

LEM is the *liquidus* and therefore it corresponds to line B on Figure 9. (Look back at the definition of the liquidus if you are unsure of this point.)

2   *Solid-and-liquid field*   While Figure 9 has only one such field, there are two fields representing the *co-existence* of liquid *and* solid in Figure 12b. If a sample plots in the left-hand field (LJE), the crystals have composition of 100 per cent G and the liquid has a composition that plots on the line LE. Conversely, if a sample has a bulk composition that is richer in H and plots in the right-hand field (MKE), the crystals have composition of 100 per cent H and the liquid plots on the line ME.

Remember that whereas on a diagram of temperature against composition the total sample may plot *in* a solid-and-liquid field, the actual crystals and liquids *never* do—they always plot on the *boundaries* to such fields. (Compare Figures 11 and 12b.)

From the definitions of solidus and liquidus you know that fields where solids and liquids co-exist must be bounded by the liquidus on their high-temperature side and by the solidus on their low-temperature side, lines B and A respectively on Figure 9.

On Figure 12b, the liquidus is represented by the curve LEM. Can you therefore work out which line(s) represent the solidus?

The most obvious part of the *solidus* is the line JEK—we have already said that it marks the temperature below which all mixtures of G and H are completely solid. However, the lines LJ and MK also represent compositions of solid material (crystals) so the complete solidus on Figure 12b consists of the lines LJ, JEK, KM.

3 *The solid-only field* Below the solidus no liquid is present and the sample is completely solid. For samples of 100 per cent G or 100 per cent H this occurs at temperatures below those at points L and M respectively. For all other samples, which are mixtures of G and H, the solid-only field occurs below the temperature corresponding to the line JEK.

Finally, there is one feature on Figure 12b that was not apparent on the phase diagram of pressure against temperature (Figure 9); it is represented by the point E. In the construction of Figure 12b, it was emphasized that the last drops of liquid remaining before samples 1 and 2 solidified completely had a composition of 60 per cent H, 40 per cent G, and were at temperature T_6: that is, they plotted at point E. Moreover, it was *only* when the liquids were at point E that crystals of both G and H formed together. *Point E is unique in that it is the only place on the diagram where crystals of G, crystals of H, and the liquid may co-exist in equilibrium.* It is called the *eutectic point*; the liquid that co-exists in equilibrium with crystals at E has a unique composition and is called the *eutectic liquid*; and systems (such as G–H) that contain an eutectic point are referred to as *eutectic systems*.

eutectic point
eutectic liquid
eutectic system

Study comment The significance of the eutectic point is also demonstrated, using the phase rule, in Appendix 1, part (ii), which you should now read.

We have now constructed a phase diagram of temperature against composition for the two-component eutectic system G–H at a particular pressure and we have discussed its general features which apply to all such diagrams of eutectic systems. The final step is to use the completed diagram to predict the melting and crystallization history of a particular sample. This is how most Earth scientists use phase diagrams, since we have neither the time nor the laboratory facilities to undertake the relevant experiments.

3.3 Crystallization and melting paths

We have introduced phase diagrams by discussing how they are determined experimentally, that is, one experimental run is represented by a single point on a phase diagram and the phase boundaries are then drawn in between the assembled points (Figures 5, 8, 9, 10 and its answer, Figure 70). In the natural situation, however, things happen *continuously* rather than as a series of 'jumps' from one experimentally determined point to another.

Thus we must become familiar with using phase diagrams to decribe the continuous chain of events that take place in a system when the physical conditions change. Perhaps the temperature rises and melting occurs: a *melting path* is then the route taken by the liquid and the crystals on a particular phase diagram during melting. Conversely, a *crystallization path* describes what happens as a liquid is cooled and solidification occurs (this is also illustrated in TV 06).

melting path

crystallization path

Many basaltic igneous rocks contain 40–50 per cent of calcium-rich plagioclase, *anorthite* ($CaAl_2Si_2O_8$), and the calcium-rich *pyroxene*[A] mineral *diopside* ($CaMgSi_2O_6$), and they have therefore been the subject of a considerable amount of

anorthite   diopside

experimental work. A common approach is to study pure compounds such as anorthite and diopside and so understand their phase relations, before trying to carry out experiments on natural rocks. This is simply because a system with only two pure minerals is comparatively easy to understand and as soon as more elements are added, more minerals may form and even the existing ones will become less pure, so the system becomes very much more complicated. The philosophy is to understand simple systems and particularly the *principles* they illustrate, before grappling with more complex ones.

Figure 13 depicts the phase relations between diopside and anorthite as determined experimentally at atmospheric pressure. There is no solid solution between diopside and anorthite (usually abbreviated to Di and An respectively), and the form of their phase diagram is similar to those for other two-component eutectic systems (for example, Figure 12b). We shall discuss what happens during the crystallization of a sample with 80 per cent An and 20 per cent Di.
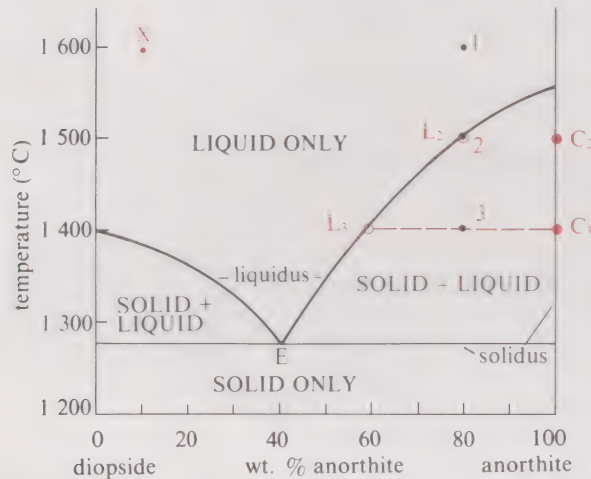
FIGURE 13   The diopside (Di)–anorthite (An) system.

At 1 600 °C, a sample with 80 per cent An and 20 per cent Di plots at point 1 on Figure 13 and is in the liquid-only field. As the temperature falls the sample remains entirely liquid until it reaches the liquidus.

Where on Figure 13 does this sample first arrive at the liquidus?

At point 2, and this is when the first crystals appear. As in Figure 11, the crystals cannot have the same composition as the liquid, but must be either 100 per cent Di or 100 per cent An. This sample is very much richer in An (80 per cent) and thus the first crystals are crystals of 100 per cent An (at C_2).

As the temperature continues to fall, more and more crystals of An are formed. Let's pause at a temperature of 1 400 °C and see what has happened to the composition of the liquid meanwhile.

At 1 400 °C, our total sample plots well in the (right-hand) solid-and-liquid field at point 3. But remember that we emphasized that while the total sample may plot *in* such a field, the co-existing crystals and liquid *never* do—they plot on the boundaries around it. Thus, since the crystals and liquid are also at 1 400 °C, the crystals plot on the solidus at C_3, and the liquid plots on the liquidus at L_3. Between L_2 and L_3 the liquid has become richer in Di because crystals of pure An have been forming.

A useful convention on phase diagrams is to draw *tie-lines* between phases that co-exist at any one time. Thus the dashed line C_3L_3 is a tie-line illustrating that at 1 400 °C, crystals of 100 per cent An co-exist with a liquid of composition L_3. Moreover, since only *two* phases exist at this temperature, the composition of the total sample (at point 3) must also lie on the tie-line—it must lie between L_3 and C_3.

tie-line

What happens as the temperature continues to fall below 1 400 °C?

More and more crystals of An are formed and the liquid becomes richer in Di (see also Figure 11).

This continues until the temperature is at 1 275 °C, whereupon the liquid is at the eutectic point E, and consists of 40 per cent An, 60 per cent Di. Liquid may only occur in the liquid-only field or on the liquidus (depending on whether it is on its own or in equilibrium with crystals), so it should be clear from the shape of the liquidus curve on Figure 13 that liquid cannot be present at temperatures below 1 275 °C. At 1 275 °C, crystals of Di start to form and crystallization of both Di and An continues at the same temperature until no liquid remains. During this crystallization, of course, the composition of the liquid does not change either. Since no material has been added to, or lost from, the total sample during crystallization, the final solid must also consist of 80 per cent An, 20 per cent Di.

ITQ 6 At 1 600 °C, a sample consisting of 10 per cent An and 90 per cent Di plots at point X on Figure 13.

(a) What is the composition of the first crystals to form as this sample cools?

(b) After further cooling, the composition of the liquid reaches 25 per cent An. Draw on the tie-line linking the composition of the liquid, the crystals, and the total sample that co-exists at that time.

(c) Are tie-lines always horizontal on phase diagrams of temperature against composition (for example, Figure 13)?

(d) At what point will crystals of An and Di crystallize together from this liquid, and what is the temperature at this point?

(e) What is the composition of the final solid?

In a eutectic system like that in Figure 13, melting is simply the reverse of crystallization. On heating our sample of 80 per cent An, 20 per cent Di, the first liquid appears when the temperature reaches 1 275 °C. That liquid must be at the eutectic point E and therefore must have a composition of 40 per cent An, 60 per cent Di (Figure 13). Since E is the only point on this diagram where crystals of Di, crystals of An, and the liquid can co-exist in equilibrium (see the previous discussion of crystallization, and the discussion of the phase rule in Appendix 1), the liquid must remain at E until all the crystals of either An or Di have melted.

In a sample of 80 per cent An, 20 per cent Di, will all the crystals of Di melt before those of An—or vice versa?

Because this sample is richer in An than the eutectic mixture (at E), all the crystals of Di will melt first. Moreover, irrespective of how much extra heat is added, the liquid will remain at E, and the temperature will stay at 1 275 °C, until all the Di has melted. It is directly analogous to the kettle of boiling water staying at 100 °C until all the liquid water has boiled off.

Once the crystals of Di have melted, the temperature can rise, and as it does so the liquid migrates up the liquidus curve—becoming richer and richer in An as more crystals of An melt. This continues for as long as the *total* sample remains in the solid-and-liquid field (i.e. two phases are co-existing). When all the crystals of An have melted, the total sample leaves the solid-and-liquid field, and since only one phase remains (the liquid) it crosses the liquidus and moves into the liquid-only field. For the sample with 80 per cent An, 20 per cent Di, the last crystals of An melt at 1 500 °C when the liquid is at L_2 and the total sample is at position 2 (Figure 13).

Study comment You should now turn to Appendix 1, part (iii), where the melting of this sample of 80 per cent An, 20 per cent Di is briefly discussed, using the phase rule.

Finally, it is important that we should be able to interpret the textures of igneous rocks in terms of the phase relations determined in the experimental laboratory. Figure 14 presents photomicrographs of three basalts that contain crystals of diopside and anorthite-rich plagioclase feldspar, and to a first approximation these may be interpreted using the Di–An system (Figure 13). (Remember that plagioclase feldspar crystals are unlikely to be pure anorthite because there is continuous solid solution between albite and anorthite; Block 1, Figure 37.)

The basalt in Figure 14a has large phenocrysts of anorthite-rich feldspars in a fine-grained groundmass that includes small crystals of diopside and plagioclase feldspar. We argued in Section 1 that such a texture suggests that the large crystals grew slowly *before* the groundmass minerals crystallized rapidly—presumably when the basalt was erupted on the Earth's surface. In terms of the
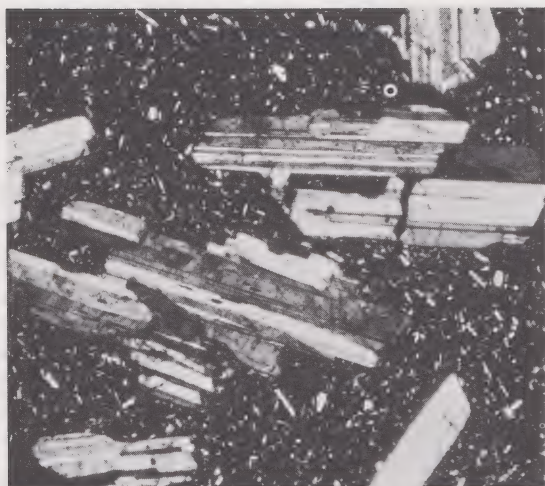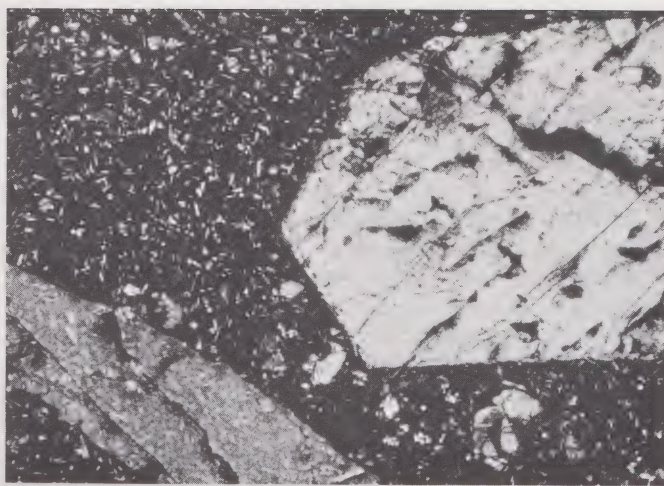
(a)   (b)   (c)

FIGURE 14 (a) Phenocrysts of anorthite-rich plagioclase feldspar in fine-grained diopside-bearing basalt (magnification × 12).

(b) Phenocrysts of diopside in fine-grained plagioclase-bearing basalt (magnification × 10).

(c) Co-existing phenocrysts of both anorthite-rich feldspar and diopside (magnification × 18).

diopside–anorthite phase diagram, such a sample must have been in the solid-and-liquid field as those early crystals of plagioclase grew. From Figure 13 we may therefore conclude that at that time: (i) the total sample was somewhere in the right-hand solid-and-liquid field and the liquid (which is now groundmass) was on the boundary to that field (the liquidus), (ii) the temperature during anorthite crystallization was therefore between 1 550 °C and 1 275 °C, and (iii) the total sample contained relatively more anorthite than diopside, otherwise diopside would have crystallized first.

ITQ 7 (a) Figure 14b contains phenocrysts of diopside set in a fine-grained groundmass. What can you say about the proportions of anorthite to diopside in the total rock and the temperatures over which the diopside could have crystallized (Figure 13)?

(b) The texture in Figure 14c suggests that anorthite and diopside *crystallized together*. From Figure 13, what are the proportions of anorthite to diopside, and at what temperature did these two minerals crystallize together?

3.4 Eutectic behaviour on icy roads

As we discuss various aspects of the phase relations of rocks and minerals it is important to remember that phase diagrams can also have a much more immediate relevance. Here is a commonplace example. Salt (NaCl) and water are two substances which when mixed together in the system NaCl–H_2O have phase relations broadly similar to those of the simple eutectic systems we have just considered (Figures 12 and 13). A mixture of NaCl and H_2O (ice) will start to melt at temperatures *below* the melting points of pure H_2O (0 °C) and pure NaCl (800 °C). This is why salt is scattered on icy roads to encourage melting.

Part of the phase diagram of temperature against composition for the system NaCl–H_2O, at atmospheric pressure, is reproduced in Figure 15. It allows us to tackle several problems which may become all too relevant if the roads freeze again this winter!

ITQ 8 (a) If your roads were covered in various mixtures of salt and water, what is the lowest temperature at which liquid could still be present and what is its composition?

(b) At what temperature do the first crystals appear if you cool a mixture of 40 per cent NaCl, 60 per cent H_2O? What is the composition of those first crystals? Assuming that they were properly mixed, would the addition of 40 per cent NaCl melt the ice on the roads at −10 °C?

(c) If the temperature is −10 °C, how much salt must be added, per 100 g of ice, to cause complete melting? Assume that the ice and salt mix thoroughly.
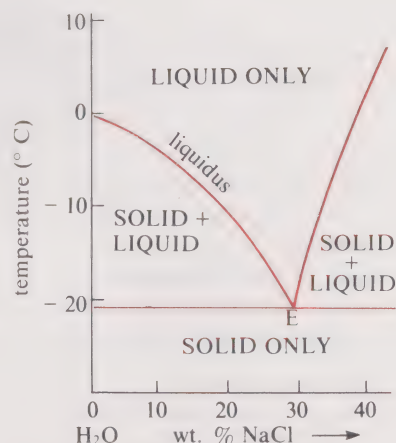

FIGURE 15 A portion of the NaCl–H_2O system.

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3.5 Summary of Section 3

In this Section we have looked at simple phase diagrams of temperature against composition for systems consisting of two components between which there is no solid solution. Such diagrams contain three different fields: liquid-only, solid-and-liquid and solid-only. It was emphasized that while a total sample may clearly plot *in* a solid-and-liquid field, the co-existing crystals and liquid *never* do—they plot on the phase boundaries around such fields, the *solidus* and *liquidus* respectively. Moreover, because there is no solid solution, the crystals can only have the composition of one or other of the two components (for example, Di and An, Figure 13; H_2O and NaCl, Figure 15). The *eutectic point* marks the composition and the temperature of the first liquid to form as the temperature rises and the last to crystallize as the temperature falls. It is fixed for any system at a particular pressure and it applies to all samples in that system, that is, any mixture of the two components. Finally, phase diagrams for the relevant two-component eutectic systems have been used to interpret textures observed in basic igneous rocks and to discuss the relations between H_2O and salt (NaCl) on icy roads.

3.6 Objectives for Section 3

Now that you have completed Section 3, you should be able to:

1 Define in your own words, or recognize valid definitions of, the terms flagged in the margins of this Section.

6 Recognize and be able to explain the significance of the main features of a two-component eutectic phase diagram.

7 Use a phase diagram to describe the crystallization and melting behaviour of a sample made up of a mixture of two components between which there is no solid solution.

8 Discuss conditions at different locations on such phase diagrams in terms of the phase rule (Appendix 1).

9 Interpret textures in suitable igneous rocks in terms of crystallization paths on a eutectic phase diagram.

Apart from Objective 1, to which they all relate, the five ITQs in this Section test these Objectives as follows: ITQ 5: Objectives 6 and 7; ITQ 6: Objective 7; ITQ 34 (Appendix 1): Objective 8; ITQ 7: Objective 9; ITQ 8: Objectives 6 and 7.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 5 (*Objectives 1 and 6*) Are the following statements correct or incorrect?

(a) For samples that do *not* have the same composition as that of the eutectic point, the liquid-only field is the only area on the phase diagram for a simple eutectic system where the liquid has the same composition as the total sample.

(b) In a simple eutectic system the first crystals to form on cooling have the same composition as the initial liquid.

(c) On phase diagrams the solid-and-liquid field(s) lie(s) between the solidus and the liquidus curves.

(d) In a simple two-component eutectic system the first liquid to form (on melting) at any particular pressure always has the same composition—regardless of the composition of the original solid.

(e) From Figure 15 we can see that crystals of ice and NaCl exist *together* at temperatures between 0 °C and −20 °C.

(f) Once a crystallizing liquid reaches the solid-only field in a simple eutectic system, then the individual crystals will have the same composition as the total sample.

(g) If only two phases are present at any particular temperature, then on a phase diagram of temperature against composition the composition of the total sample must lie on the *tie-line* between those two phases.

SAQ 6 (*Objective 7*) Using Figure 13, describe briefly what happens as a sample of 80 per cent diopside and 20 per cent anorthite is cooled from 1 600 °C to 1 200 °C. Pay particular attention to the temperature at which the first crystals appear and to their composition; and also to the composition and temperature of the last drop of liquid before solidification is complete.

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SAQ 7 (*Objective 9*)   With reference to Figures 13 and 14 and SAQ 6, describe the textures you would expect to find if three samples of 80 per cent diopside, 20 per cent anorthite (as in SAQ 6) were quenched, having first cooled slowly to the following temperatures: (i) 1 500 °C; (ii) 1 350 °C; (iii) 1 200 °C.

4   Some simple systems involving minerals inter-related by solid solution

In Section 3 we considered crystallization and melting in systems in which the components (or minerals) had *fixed* compositions even though the liquid composition changed during crystallization. However, many minerals of geological importance do not have fixed compositions, but belong to systems in which *any* composition between two end-member minerals can exist in the natural state. These are called *solid-solution*[A] systems or *series*.

Solid-solution series were discussed earlier in the Course in the context of the rules governing elemental substitution of different elements into crystal structures. A simple example is the olivines, where the two end-members are magnesium olivine (Mg_2SiO_4, *forsterite*)[A] and iron olivine (Fe_2SiO_4, *fayalite*)[A]. Natural olivines very rarely have the composition of these pure end-members, but vary continuously by the substitution of Fe^{2+} for Mg^{2+}. A more complex solid-solution relationship is that of the *plagioclase feldspars*, which vary in composition between *albite* ($NaAlSi_3O_8$) and *anorthite* ($CaAl_2Si_2O_8$) by the *coupled substitution*[A] of (Ca^{2+}, Al^{3+}) for (Na^+, Si^{4+}). The form of their respective phase diagrams is very similar and we shall illustrate them using the diagram of temperature against composition for the plagioclase feldspars (Figure 16).

albite
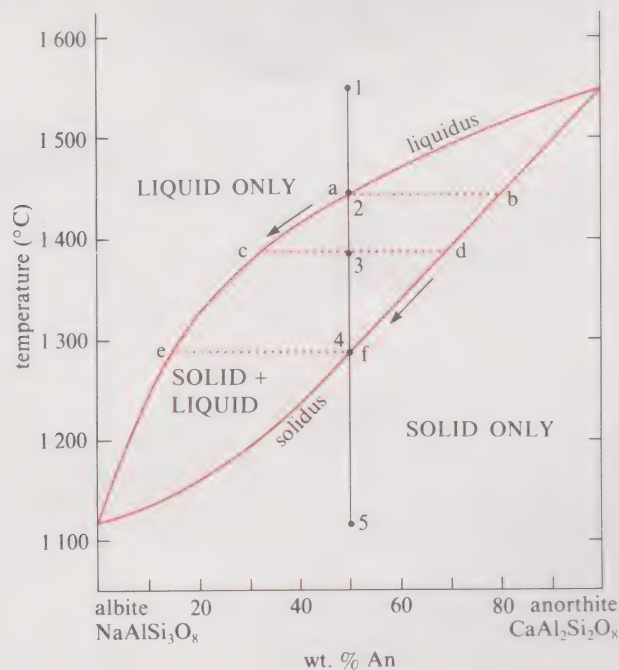
FIGURE 16   Phase diagram of temperature against composition for the plagioclase feldspar system with solid solution between albite and anorthite. The line connecting the dots 1, 2, 3, 4, 5 represents the cooling (or heating) path of the total sample of composition An_{50} discussed in the text. The horizontal dotted lines are tie-lines linking the crystals and liquid that co-exist on the solidus and liquidus respectively at a particular temperature.

4.1   The plagioclase feldspar system

The diagram of temperature against composition in Figure 16 has many similarities to those plotted previously for eutectic systems (Figures 12 and 13, for example). The horizontal axis again illustrates variations in composition, this time between 100 per cent albite and 100 per cent anorthite, and it was constructed using the same quenching technique. In detail it contains the same five features, the liquid-only field, the solid-only field, the solid-and-liquid field, the solidus and liquidus; and these still have exactly the same definitions and properties as they did in the earlier diagrams (for example, Figures 9 and 12). It is only their shape, or form, that has changed: in particular, there is only one solid-and-liquid field.

The simplest way to understand a new phase diagram is to use it. So, let us take a liquid that consists of 50 per cent albite and 50 per cent anorthite and look at its crystallization path as it cools. Note that for plagioclase feldspars, 50 per cent anorthite is written conventionally as An_{50}.

At $1\,550\,°C$, our sample (An_{50}) plots at point 1 in the liquid-only field (Figure 16). As the temperature falls it intercepts the liquidus at point 2 and the first crystals begin to form. Our sample has thus entered the solid-and-liquid field and, in exactly the same way as in all the previous diagrams of temperature against composition, neither the crystals nor the liquid plot *in* this field, but rather on the boundaries around it. Since we may assume that they are both at the same temperature as the total sample ($1\,445\,°C$, point 2) the liquid plots on the liquidus at point a and the crystals plot on the solidus at point b. The line a–b is the tie-line between the co-existing crystals and liquid; and since they are both at the same temperature, the tie-line must be horizontal.

The composition of the plagioclase feldspar that plots on the solidus at a temperature of $1\,445\,°C$ (point b) may be read off the horizontal axis and is about An_{80}. The composition is *not* pure anorthite (An_{100}) because these crystals are part of a solid-solution series in which all compositions between 100 per cent Ab and 100 per cent An can exist in solid form. In this case (at point b), they are a mixture of 20 per cent albite and 80 per cent anorthite (An_{80}).

> Are these crystals richer or poorer in anorthite than the co-existing liquid? What effect does the formation of such crystals have on the proportions of albite to anorthite in the remaining liquid?

The crystals are richer in anorthite than the liquid. Formation of such crystals therefore impoverishes the liquid in anorthite so that the liquid becomes relatively enriched in albite, that is, it moves to the left on Figure 16.

> So what happens to our sample as the temperature falls below $1\,445\,°C$ to say $1\,385\,°C$?

The sample is now almost in the centre of the solid-and-liquid field (point 3, Figure 16) and again the crystals and liquid do not plot in this field, but on the solidus and liquidus respectively. At the temperature of $1\,385\,°C$ the liquid therefore plots at point c and the crystals plot at point d. As predicted, the formation of crystals rich in anorthite has made the remaining liquid richer in albite—it now has a composition of about An_{32} (that is, 68 per cent albite, 32 per cent anorthite).

But what about the crystals? In all the other systems we have looked at the compositions of the minerals were fixed and could not change. However, in this example, the crystals of plagioclase feldspar have changed in composition from An_{80} at $1\,445\,°C$ (point b) to An_{68} at $1\,385\,°C$ (point d). How can that happen?

You may remember that chemical equilibrium is not a static situation like mechanical equilibrium (for example, a glass on a horizontal table). Rather, it is a state of *dynamic balance* between opposing processes. Thus, if crystals and liquid are to remain in equilibrium in the plagioclase system, there must be continuous *reaction* between them, so that at any one temperature *all* the crystals have a unique composition given by the corresponding point on the solidus in Figure 16. For example,

at $1\,445\,°C$ $\qquad\qquad$ An_{80} (solid) $\rightleftharpoons$ An_{50} (liquid) $\qquad\qquad$ (2)

Remember that anorthite (An_{100}) is $CaAl_2Si_2O_8$ and that albite (An_0 on Figure 16) is $NaAlSi_3O_8$. If they are rewritten

$$CaAl(AlSi_2O_8)$$

and $\qquad\qquad\qquad\quad$ $NaSi(AlSi_2O_8)$

you can see that they both have $(AlSi_2O_8)^{5-}$ in common, but differ in that anorthite also contains Ca^{2+} and Al^{3+}, whereas albite contains Na^+ and Si^{4+}. Reactions between crystals and liquid, as in equation 2, therefore involve exchange between (Ca^{2+}, Al^{3+}) and (Na^+, Si^{4+}); that is, coupled substitution. At equilibrium at $1\,445\,°C$, the crystals (An_{80}) contain 80 per cent of (Ca^{2+}, Al^{3+}) and only 20 of (Na^+, Si^{4+}) while the liquid (An_{50}) contains approximately equal proportions of each.

However, this equilibrium is very sensitive to temperature and thus, by the time the sample has cooled to 1 385 °C (point 3), the equilibrium between solid and liquid has become

$$An_{68}(s) \rightleftharpoons An_{32}(l) \qquad\qquad (3)$$
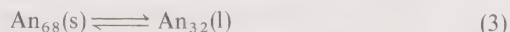
Thus the balance between the proportions of (Ca^{2+}, Al^{3+}) and (Na^+, Si^{4+}) in the crystals compared with that in the liquid has shifted dramatically with the fall in temperature from 1 445 °C to 1 385 °C. Moreover, the fact that the liquidus and solidus are smooth curves on Figure 16 indicates that these changes have taken place *continuously*—we could write a different equilibrium equation for every temperature between 1 445 °C and 1 385 °C.

For these exchange reactions to take place between the crystals and the liquid so that the composition of both can change continuously on cooling, the ions must be able to diffuse through the solid crystals.

This takes time, and if cooling is too fast there may be insufficient time for the crystals to reach equilibrium with the liquid. Some of the consequences of non-equilibrium are discussed in Section 4.2.

Returning to our sample in Figure 16, as the temperature falls below 1 385 °C (point 3), the compositions of the crystals and the liquid move down temperature along the solidus and the liquidus. Both become richer in albite, until at 1 290 °C (point 4), *the composition of the crystals (point f) is the same as that of the original sample* (An_{50}).

> The bulk composition of the sample hasn't changed, yet *both* the crystals and the liquid have become richer in Ab. How can this happen? Surely if one is getting richer in albite, the other must be getting richer in anorthite?

The answers lie in the relationship between the compositions of the co-existing crystals and liquid *and their proportions*. At higher temperatures, compositions of both are relatively rich in An and there are comparatively few crystals; at lower temperatures the crystals and liquid are both richer in Ab but only a small proportion of the sample is still liquid. This is explained in more detail after ITQ 9.

Returning to the sample at point f in Figure 16: since the crystals have the same composition as the original sample (An_{50}), and assuming that nothing has been added to or removed from the sample, it follows that there cannot be any liquid remaining. Thus at 1 290 °C (point 4) the sample has become entirely solid and crystallization is complete.

To put it another way, when the cooling path of the *total* sample (1, 2, 3, 4, and so on in Figure 16) intersects the solidus (point 4), the sample moves from the solid-and-liquid field to the solid-only field. There can be no liquid left.

> **ITQ 9** A sample of molten plagioclase feldspar has a composition of An_{70}. Use Figure 16 to answer the following questions:
>
> (a) How much albite does this sample contain? (Give your answer in weight per cent.)
>
> (b) What is the temperature at which the first crystals appear?
>
> (c) What is the composition of the first crystals to form?
>
> (d) What is the composition of the *total* sample after half of it has crystallized?
>
> (e) At what temperature does the sample become completely solid?
>
> (f) What is the composition of the last drop of liquid before crystallization is complete?
>
> (g) What is the composition of the crystals in equilibrium with that last drop of liquid?

We should now return to those queries about how the liquid and the crystals in the plagioclase system *both* manage to become richer in albite as the temperature falls. However, to obtain a satisfactory answer we need to be able to calculate the proportions of crystals and liquid which are present together at any particular temperature.

Consider a sample that plots within the solid-and-liquid field (S in Figure 17). At a particular temperature we may read off the compositions of the crystals (C) and the liquid (L) from the solidus and liquidus. Then if we know the composition of the total sample, we can calculate the relative proportions of the sample present as crystals and liquid in equilibrium at that temperature. If C and L are equidistant from S, as they are in Figure 17, it follows that S must contain equal amounts of C and L, that is, it is 50 per cent crystals, 50 per cent liquid. Similarly, if the bulk composition of the sample is close to the composition of one of the two phases (crystals or liquid), then the one to which it is closest must be present in the largest amount. It is possible, therefore, to measure the distances along the tie-line from the bulk sample S to each of the phases (C and L) and to determine the relative amount of each phase present. In Figure 17, the length LS is a measure of the relative amount of crystals C, and CS is a measure of the relative amount of liquid L.

FIGURE 17 A sketch of the Ab–An system to illustrate how to calculate the relative proportions of crystals C and liquid L in a total sample S (see text).

Thus
$$\frac{\text{relative amount of crystals}}{\text{relative amount of liquid}} = \frac{LS}{CS}$$

or
$$\text{percentage of crystals } C = \frac{LS}{LC} \times 100$$

and,
$$\text{percentage of liquid } L = \frac{CS}{LC} \times 100$$

Applying this technique to the sample in Figure 16, how much of that sample has crystallized at 1 385 °C (point 3)?

$$\text{percentage of crystals} = \frac{c3}{cd} \times 100$$

$$= \frac{12\,\text{mm}}{24\,\text{mm}} \times 100$$

$$= \tfrac{1}{2} \times 100$$

$$= 50$$

At 1 385 °C, the sample An_{50} consists of 50 per cent crystals and 50 per cent liquid.

ITQ 10 Using the method outlined above, calculate how much of the sample An_{50} (Figure 16) has crystallized at 1 435 °C (10 °C below the temperature at point 2). Express your answer as a percentage of the total sample.

The conditions described in ITQ 10 are similar to those of point 2 in Figure 16; the answer illustrates that at this stage crystallization has only just started and there are comparatively few crystals. Thus, even though they are rich in anorthite, their formation has had little effect on the composition of the liquid, which is still very similar to that of the total sample. Conversely, at point 4 (Figure 16) only a few drops of liquid remain (at e) and the composition of the co-existing crystals (at f) is therefore very similar to that of the total sample.

Between points 2 and 4 both the liquid (a ⟶ e) and the crystals (b ⟶ f) have become richer in albite. This is because, despite their own trends to more albite-rich compositions, the crystals are always richer, and the liquid is always poorer in anorthite than the bulk sample. As more and more crystals form, their compositions get closer to that of the bulk sample, that is, they become richer in albite. Meanwhile, the liquid is being depleted in anorthite so that as its volume shrinks its composition moves further and further from that of the bulk sample—and it is also getting richer in albite (a ⟶ e).

Throughout this discussion we have assumed that complete equilibrium was maintained between the crystals and the liquid. Let us look now at what happens if complete equilibrium does not occur.

4.2 Equilibrium or non-equilibrium?

In our discussion of the plagioclase system (Figure 16), it was assumed that complete equilibrium was maintained between the crystals and the liquid and it was emphasized that both changed in composition as the temperature fell. This was possible because the plagioclase feldspars are a solid-solution series and equilibrium was maintained through continuous reaction between the crystals and the liquid. Such reaction actually takes place at the edges of the crystals (where the crystals and the liquid are in contact). For reactions to occur and for equilibrium to be
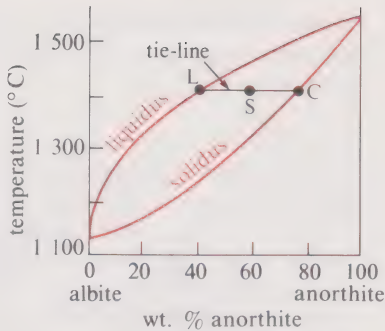
maintained, the various ions involved (for example, Ca^{2+}, Al^{3+}, Na^+ and Si^{4+}; see Section 4.1) must be able to move freely to and from the crystal edges. In both crystals and liquid such movement usually takes place by diffusion but, as you might expect, it takes very much longer in a solid crystal than in a liquid, and in the latter movement may also be speeded up by mixing or *convection*[A] (this will be discussed in Block 4).

The rate at which ions diffuse depends not only on the material through which they are passing, but also on the temperature and how the concentration of the element varies within the material. The relations between these factors are complex but, for example, it has been calculated that it might take up to 40 000 years for the Ca in a spherical crystal 1 cm in diameter to equilibrate with that in a well-mixed, homogeneous liquid at 1 000 °C.

By contrast, if no liquid is present, adjacent minerals may not equilibrate with one another even after billions of years. This is particularly true at low temperatures and it is just as well for those of us who wish to study igneous processes, since one consequence of extremely slow diffusion is that mineral compositions, which may reflect reactions at over 1 000 °C, are still preserved at room temperatures.

If equilibrium has been maintained during cooling in the plagioclase system, then all the crystals should have the same composition and they should be homogeneous (that is, there should be no chemical variations between or within individual crystals).

Note that to describe a crystal as *homogeneous* does not necessarily imply that it is 'pure'. A crystal of 100 per cent anorthite consists purely of anorthite and we may assume that it is homogeneous. However, a crystal of An_{50} is obviously made up of albite and anorthite (50 per cent of each) and yet it is homogeneous if everywhere in the crystal the composition is An_{50}.

Homogeneous crystals are often found in large igneous intrusions which we know must have cooled slowly. However, in many igneous (particularly volcanic) rocks the plagioclase crystals are often spectacularly *zoned* (Figure 18), with compositions which may be as much as An_{80} in the centre passing through progressively more albite-rich layers to rims which may consist of only An_{30}. Where such zoned crystals occur, it is fairly clear that the equilibrium between the liquid and the inner portions of the crystals has not been fully maintained during cooling. As the crystal grew, its surface was presumably in equilibrium with the liquid, but the inner parts of the crystal became isolated from the liquid and there was insufficient time for them to re-equilibrate with the liquid as the temperature fell. Equilibrium was only 'skin-deep'!

In summary, equilibrium is maintained by continuous reaction between crystals and liquid. Such reaction occurs where both are in contact, and non-equilibrium results if there is insufficient time for ions to move to and from the edges of the crystals. The shortage of time might reflect rapid cooling, or alternatively the crystals may have been removed physically before they had time to re-equilibrate with the liquid. Let us now compare the effects of non-equilibrium and equilibrium crystallization in simple eutectic and solid-solution systems.

The eutectic systems we have looked at (Figures 11–13 and 15) involved substances of *fixed* composition. Thus, no matter whether the whole crystal is actually in equilibrium with the liquid or not, the compositions of the crystals remain the same and there is no opportunity for inhomogeneous crystals to form. A similar argument can be made for the liquid.

In all eutectic systems the composition of the liquid remains constant during cooling until the first crystals appear. Then, since the composition of the crystals is different from that of the liquid, the latter changes towards that at the eutectic point (E in Figure 12) as more and more crystals form. Since the crystals are of the same fixed composition whether they are in equilibrium with the liquid or not, the path followed by the composition of the liquid must also be the same during equilibrium and non-equilibrium crystallization.

By contrast, if the crystals are not in complete equilibrium with the liquid in a *solid-solution system* such as the plagioclase feldspars, then this affects the composition of both the crystals and the liquid. Under equilibrium conditions, complete crystallization of the sample illustrated in Figure 16 results in homogeneous
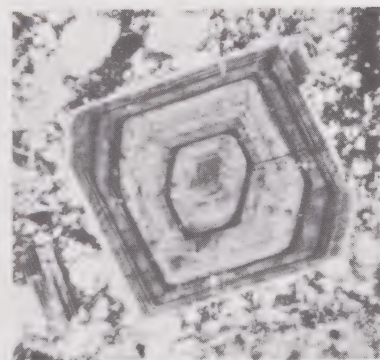
zoned crystals

FIGURE 18   A zoned plagioclase crystal. The concentric lines represent boundaries between layers of different composition. The crystal becomes progressively richer in albite towards the rim.

plagioclase crystals that have the same composition as the starting material (An_{50}). However, in that example, the first crystals to form are An_{80}, and even after 50 per cent crystallization they are only An_{68}.

> What would happen to the composition of the liquid if crystals of An_{68} (point d on Figure 16) were then isolated and prevented from re-equilibrating with the liquid at lower temperatures?

The short answer is that, since these crystals are relatively rich in anorthite, the liquid will become even more depleted in anorthite (and hence richer in albite) than in the case of simple equilibrium crystallization (Figure 16). In detail, we should be able to be a little more specific.

The diagram of temperature against composition for the plagioclase feldspar system is reproduced in Figure 19a. After 50 per cent of the sample An_{50} has crystallized under equilibrium conditions, the liquid is An_{32} (point c) and the crystals are An_{68} (point d—see also Figure 16). If equilibrium is maintained until crystallization is complete, then, as discussed earlier, the final sample will consist of homogeneous crystals of An_{50} (Figure 19b). However, if after 50 per cent crystallization all the crystals (An_{68}) become isolated from the liquid and can no longer react with it, then they have no further role to play in the evolution of the liquid, whose composition is now An_{32}. *It is now as if we were considering the evolution of a sample of An_{32}, rather than An_{50}.*
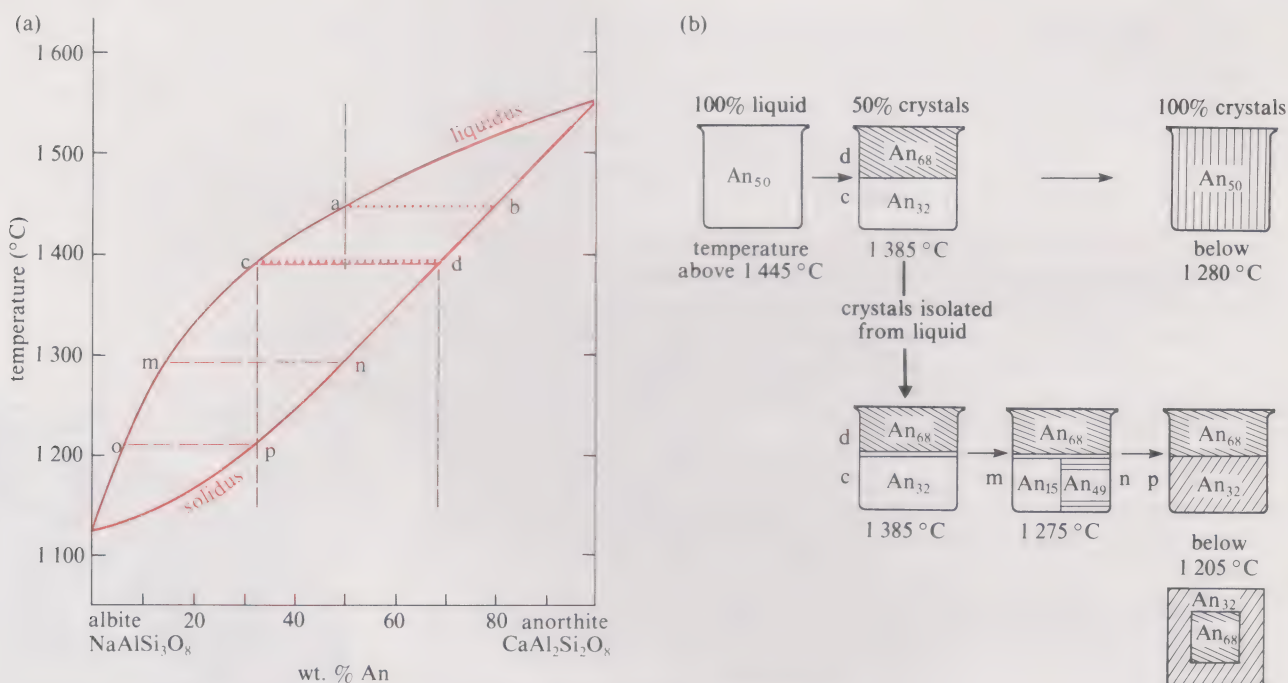
FIGURE 19   (a)   Phase diagram of temperature against composition for the plagioclase feldspar system. A sample of An_{50} crystallizes under equilibrium conditions (as in Figure 16) until 1 385 °C, whereupon the crystals (d) become isolated from the liquid (c) and cool separately. Horizontal lines are tie-lines between co-existing crystals and liquid, before (dotted) and after (dashed) the crystals and liquid were separated at 1 385 °C.

(b)   Diagrammatic sketch illustrating the crystallization of the sample of An_{50} depicted in Figure 19a. Horizontal arrows illustrate equilibrium crystallization and the vertical arrow reflects non-equilibrium (that is, the physical separation of crystals and liquid). Temperatures and letters d, c, m, n, p are from Figure 19a.

> Where in Figure 19a does a sample of An_{32} plot when the first crystals appear? What is the composition of those first crystals?

The first crystals appear when the sample plots on the liquidus, that is, at c for sample An_{32}. The first crystals plot on the solidus at the same temperature, point d, An_{68} (Figure 19a). If equilibrium is then maintained as sample An_{32} cools, then at 50 per cent crystallization the liquid plots at m (An_{15}) and the crystals plot at n (An_{49}) and, when completely solid, the sample consists of homogeneous crystals of An_{32}. It moves from the solid-and-liquid field to the solid-only field at p.

Reconsidering our initial sample of An_{50}, we can see that because crystals of An_{68} were isolated from the liquid when its composition reached An_{32}, we have ended up with a completely solid sample in which 50 per cent of the crystals are An_{68} and 50

per cent are An_{32} (Figure 19b, second row). Moreover, if this sample is represented by a sketch showing the first 50 per cent of crystals to form in the middle, we can recognize a zoning which although simpler, is similar to that in the plagioclase crystal in Figure 18. There is a 'core' in which the composition is An_{68}, surrounded by a 'rim' of An_{32} (Figure 19b). By having several stages at which the co-existing crystals and liquid were isolated from each other we could generate multiple zoning of the sort more usually observed in nature and illustrated in Figure 18.

In summary, non-equilibrium crystallization in a system involving solid solution, such as the plagioclase feldspars, results in crystals with a range of compositions. Early crystals are richer in the higher-temperature end-member (anorthite) and become preserved because they do not re-equilibrate with subsequent (lower-temperature) liquids. Such liquids are therefore relatively impoverished in the high-temperature end-member (anorthite) and on solidification they result in crystals enriched in the low-temperature end-member (albite). By repeated crystallization and separation of the sort illustrated in Figure 19, it is possible to arrive at very albite-rich liquids—and hence crystals.

>ITQ 11   Figure 20 is a diagram of temperature against composition for the olivine solid-solution system. Its form is very similar (albeit a mirror image) to that of the plagioclase feldspar system (Figures 16 and 19). Consider a sample of Fo_{60} (60 per cent forsterite and 40 per cent fayalite).
>
>(a)   Under equilibrium conditions, what are the compositions of the first and last crystals to form?
>
>(b)   After 20 per cent crystallization, the crystals are Fo_{83}. What are the temperature and the composition of the co-existing liquid?
>
>(c)   After 20 per cent crystallization, the crystals and the liquid become separated physically and can no longer react with one another. Assuming that the remaining liquid then crystallizes under equilibrium conditions, what are the compositions and percentages of the different crystals when the total sample (Fo_{60}) is completely solid?
>
>(d)   Refer to the chemical formulae for forsterite and fayalite in Figure 20. Is the Mg/Fe ratio in early-formed olivine crystals likely to be greater or less than that in crystals that form at lower temperatures?
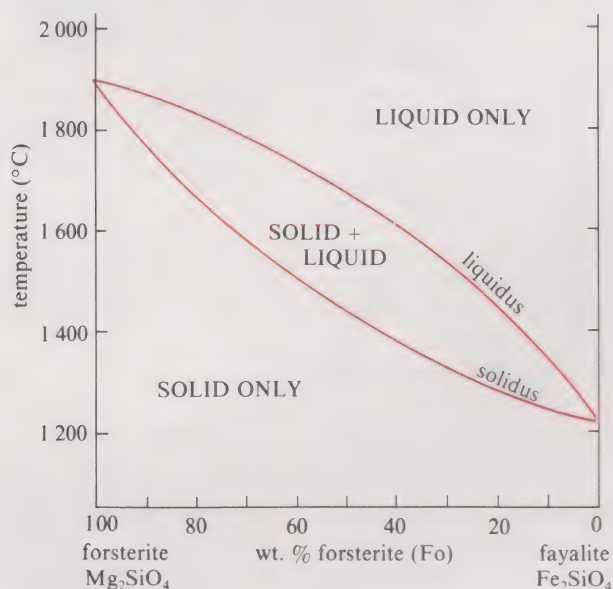
FIGURE 20   Phase diagram of temperature against composition for the olivine system in which there is solid solution between forsterite and fayalite (ITQ 11).

We have seen that, in general, non-equilibrium crystallization may take place for two reasons: first, because the temperature falls too rapidly for the inner portions of individual crystals to re-equilibrate with the later, lower-temperature liquids. This results in a range of compositions being preserved in a single crystal, as exemplified by the zoned plagioclase feldspar in Figure 18. Secondly, non-equilibrium may occur because the crystals are simply separated physically from the liquid. This is *fractional crystallization* as illustrated for olivine in Figure 4 (sample (b)); and in this case the individual crystals may be fairly homogeneous, but those that crystallized early in the sequence will be richer in the higher-temperature end-member than those that crystallized later.

An example of such large-scale variations in composition has been documented for plagioclase feldspars in igneous rocks at Skaergaard in Greenland. A large body of basic magma was intruded about 55 Ma ago and appears to have crystallized relatively slowly (that is, slowly enough for large crystals to form). Figure 21 illustrates the variation in the composition of the plagioclase crystals with height in that part of the intrusion that is presently exposed at the surface. Crystals near to the base are An_{70} and there is a striking increase in the amount of albite relative to anorthite towards the top of the intrusion. This suggests that the crystals near the base crystallized at higher temperatures (and therefore earlier) than those higher in the intrusion (see Figure 16).

So far, we have looked at simple systems containing only two mineral components and hence termed *binary systems*. Although the minerals we considered are fairly common (plagioclase, pyroxene and olivine) particularly in basaltic rocks, such rocks nearly always contain more than two minerals. To describe the chemical variation of basalts more fully, we need to be able to add another mineral and thus study three minerals together. Systems with three mineral components are called *ternary systems*.

4.3 Ternary diagrams: the diopside–albite–anorthite system

The principles involved in manipulating ternary phase diagrams are exactly the same as those with which you should now be familiar from the preceding Sections of this Block: we are simply going to add a third dimension to the diagrams. If you are ever confused by this extra dimension, make sure that you go back and re-learn the basic principles as portrayed particularly in Figures 12, 13 and 16.

The two most common minerals in basaltic igneous rocks are Ca-rich pyroxene and Ca-rich plagioclase feldspar (see for example the percentages of pyroxene and plagioclase feldspar in the *modal analysis*[A] of basalt in Block 1, Table 13). If we confine our discussion to two-component systems (as in Section 3.3 of this Block), we are forced to compromise and to discuss basalts simply in terms of the phase relations of *diopside* and *anorthite* (Figure 13). However, as illustrated on Figure 16, even Ca-rich plagioclase will be a mixture of albite and anorthite, and we can now get closer to natural rocks by considering the ternary system diopside–albite–anorthite.

To explore how these three minerals behave during crystallization, we first need to know the phase relations in the three binary systems: diopside–anorthite, albite–anorthite, and diopside–albite. We have already looked at the first two of these, and the diopside–albite system is basically the same as the diopside–anorthite system: no solid solution occurs between the two minerals and they crystallize together only at a eutectic point. The three systems are shown together in Figure 22.

This sketch of a block model shows how the diopside–albite (front face), diopside–anorthite (back face) and albite–anorthite (right-hand side) systems can be placed together. It would be possible to draw an infinite number of binary systems containing diopside and a plagioclase feldspar of any composition *between* albite and anorthite. One of these is shown for diopside and a plagioclase with equal amounts of albite and anorthite (An_{50}); it is labelled G on Figure 22.

If the liquidus curves from all these binary systems are joined together they form a *liquidus surface* which may then be drawn as a relief surface as in Figure 23.

In Figure 23, the melting points of pure albite and pure anorthite are represented by points on the 'corners' of the liquidus surface. However, the melting point of pure diopside is a horizontal line along one edge of the liquidus surface. We can therefore simplify the diagram by also considering the melting point of diopside as a single point, that is, by depicting the relations between diopside, albite and anorthite in a triangular diagram (Figure 24) rather than a rectangular one (Figure 23).

Study comment If you have any difficulty in envisaging how these three two-dimensional systems have been brought together into one three-dimensional system, make sure you watch TV 06. In the latter part of that programme a three-dimensional model is assembled from three binary eutectic systems. In addition, model 1 in your Home Experiment Kit represents the system Di–Ab–An, as sketched in Figure 24. You will find it helpful to use this model as you work through this Section and AV 05, which you should do at the end of this Section.
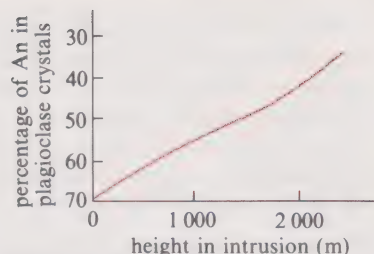
FIGURE 21 The chemical composition of plagioclase crystals at different heights in the Skaergaard intrusion.

binary systems

ternary systems
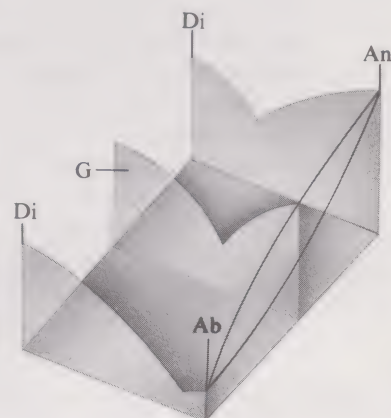
FIGURE 22 Block model showing the diopside–albite, diopside–anorthite and albite–anorthite systems. G is the binary system between Di and An_{50}.
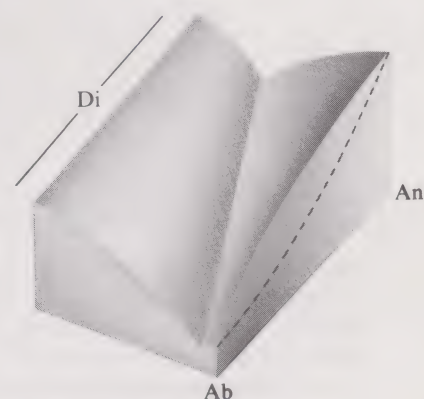
FIGURE 23 Block model of the diopside–albite, diopside–anorthite and albite–anorthite systems. The relief of the liquidus surface is shaded.
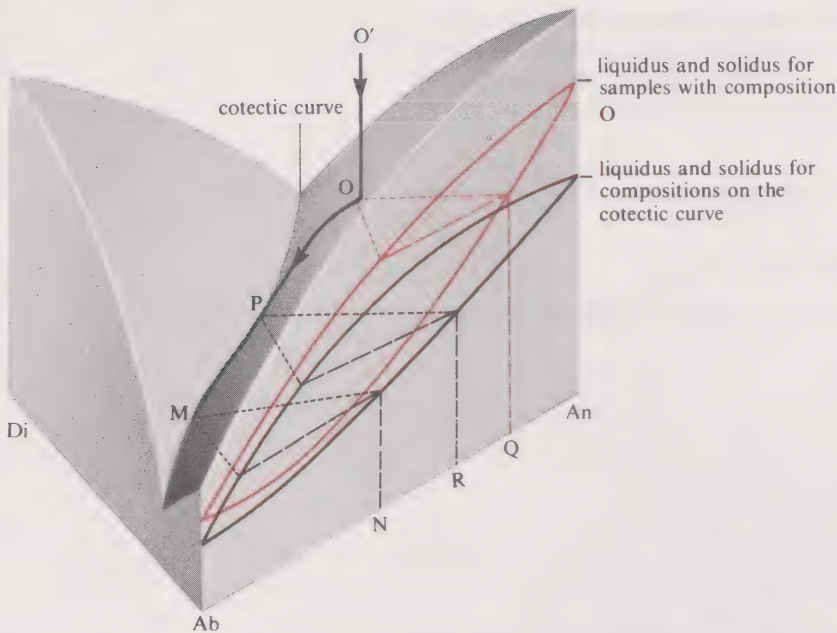
FIGURE 24 Block model showing the liquidus surface of the diopside–albite–anorthite system. (M, N, O, O', P, Q and R are explained in the text.) Note that the curves of the liquidus and the solidus *through the composition at O* and for compositions on the cotectic curve are projected onto the Ab–An face.

Compare the shape of the liquidus surface in Figure 24 with that in the rectangular block model (Figure 23) to convince yourself that they are really the same.

In the relief models the vertical direction (the relief) represents temperature. Thus, in exactly the same way that contours on maps depict the topography of the countryside, we can represent the liquidus surface by temperature contours on a plan view of the relief model. This is much more practical, and is the usual method of recording results in ternary systems (Figure 25).

On these plan-view diagrams, in the same way as on topographic maps, the spacing between contours indicates how steeply the liquidus surface slopes. In addition, you should be able to assess the shape of the valley between the diopside–anorthite and diopside–albite eutectics by looking at the distribution of the temperature contours on Figure 25. If you find this difficult, compare Figure 25 with your three-dimensional block model of this system (model 1); note in particular that the two ends of the valley are the eutectic *points* in the two-component systems of Di–Ab and Di–An, and that the valley floor slopes down (that is, down temperature) towards the diopside–albite eutectic.

How can we plot compositions in a *triangular diagram* such as Figure 25?

triangular composition diagram
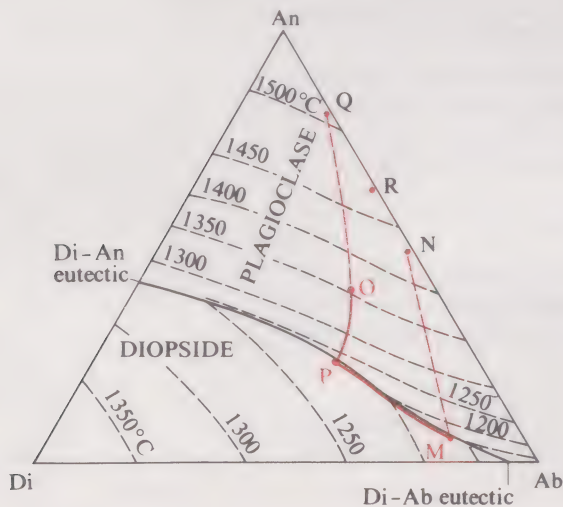
FIGURE 25 Diagram of the diopside–albite–anorthite system. (M, N, O, P, Q and R are explained in the text.) Note that this diagram contains the same data as Figure 24.

The data, in this case for three minerals, must be added together and then re-calculated as percentages. They can then be plotted directly. This is illustrated in Figure 26, where point Z represents a mixture of 70 per cent P + 10 per cent R + 20 per cent Q. Look closely at the way in which this point is plotted and then answer ITQ 12.

ITQ 12   Plot these two samples on Figure 26 (assume P = anorthite, Q = diopside and R = albite):

(i)   14 per cent Di, 43 per cent Ab, 43 per cent An.

(ii)   70 g Di, 80 g Ab, 50 g An (in this case remember to recalculate the data as percentages).
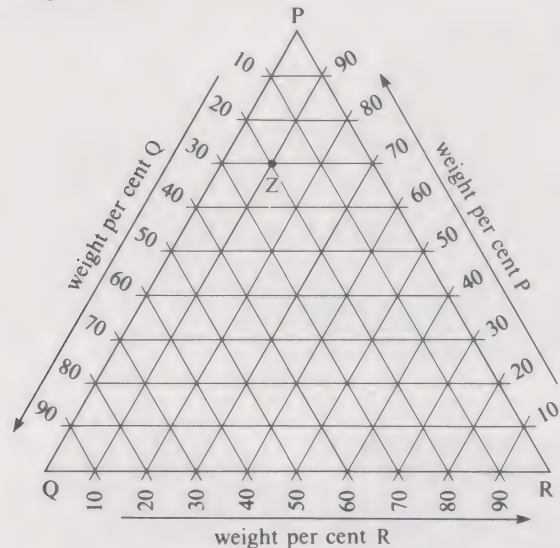
FIGURE 26   The plotting of points on a ternary diagram.

We have now looked at the ways in which a system consisting of three minerals can be represented, and how a mineral mixture of a given composition can be plotted in a diagram of such a system. We are therefore in a position to describe the *crystallization path* of a liquid (a molten rock consisting of these three minerals) as it cools and crystallizes. For this, you will need to refer to Figures 24 and 25 and model 1. We shall consider a liquid of 14 per cent Di, 43 per cent Ab and 43 per cent An, and describe its crystallization path in a series of steps (i)–(ix).

You may find these steps difficult to envisage at first and may therefore wish to read them two or three times. Remember that *no new principles are being introduced* and that it is merely a question of becoming used to thinking in three dimensions which is something that we all take a little time to get used to.

(i)   As you also showed in your answer to ITQ 12, our liquid plots at point O on Figures 24 and 25.

(ii)   Since our sample is initially entirely liquid, it is at a higher temperature than the liquidus surface for the composition O. On the relief model (Figure 24), it therefore plots above the liquidus surface somewhere on the line O'–O.

(iii)   As the temperature falls. the sample moves down the vertical line O'–O (Figure 24) until it intersects the surface at O. The temperature on the liquidus surface at O can be read off the contours on Figure 25 and it is 1 370 °C. This is clearly the temperature at which crystals begin to form from this liquid.

Which mineral crystallizes first—diopside or plagioclase?

(iv)   Because the liquid has begun to crystallize on the plagioclase side of the temperature valley in the liquidus surface, crystals of plagioclase will form first. This is analogous to the crystallization in simple eutectic systems (look back at Figures 12 and 13, pp. 19 and 21).

Remembering that our liquid has equal amounts of albite and anorthite, go back to Figure 16 and try to work out what will be the composition of the first plagioclase crystals to form.

(v)   The example in Figure 16 also had equal proportions of albite and anorthite, and thus, for the same reasons we used in Section 4.1, the first crystals will have a composition of An_{80} (Q in Figures 24 and 25).

Note that the temperature at which the first crystals form is about 1 445 °C in Figure 16 but only 1 370 °C in Figure 25—*even though the plagioclase has the same composition in each case.*

Can you suggest why that might be?

It is exactly the same effect as when salt is added to icy roads to lower the freezing point. Generally, when another component (in this case diopside) is added to a system to form a eutectic relationship, then both the liquidus and the solidus curves become depressed to lower temperatures. Thus for our sample (plotting at composition O) both the liquidus and the solidus are topographically lower, that is, they are at lower temperatures, than in the simple Ab–An system along the edge of the block model (Figure 24).

To make this easier to see we have projected the liquidus and solidus curves both for our sample at point O and for compositions on the cotectic curve (defined below) onto the pure Ab–An face of the block model. You can see how in both cases the liquidus curves are significantly lower than the liquidus curve for the pure Ab–An system (the top edge of the model). *It is most important to remember that the liquidus and solidus curves for our example at point O are applicable only to samples with that particular composition.* Samples with slightly *more* diopside will have *lower* liquidus and solidus temperatures, while those with slightly *less* diopside will have *higher* liquidus and solidus temperatures.

(vi)   As the temperature falls below 1 300 °C, more crystals of plagioclase form and, provided that equilibrium is maintained between the crystals and the liquid, both tend to become richer in albite (Figures 16 and 19, and discussion). The effect on the composition of the liquid is therefore twofold: not only is it becoming richer in albite, it is also getting richer in diopside. Moreover, when the latter happens the liquidus and solidus curves for composition O projected onto the Ab–An side of the block diagram (Figure 24) cease to be applicable. Because the liquid is getting richer in diopside (it is moving from O toward P on Figures 24 and 25), both the liquidus and solidus curves move to lower temperatures. If we were to project them all onto the Ab–An side of the block diagram there would be a continuum of liquidus and solidus curves between those shown for compositions at O and on the cotectic curve (Figure 24).

In detail, therefore, the evolution of the liquid as the temperature falls is complex because it reflects a shift to compositions richer in both albite and diopside. This causes the liquid to move in a slightly curved path from O towards the diopside field (Figure 25). As the liquid goes from O to P, the composition of the co-existing plagioclase crystals moves from Q to R (Figures 24 and 25).

Why do Q and R reflect plagioclase compositions on *different* solidus curves projected on the Ab–An side of the block diagram in Figure 25?

Because the composition of the liquid has changed between O and P; Q is read off the solidus for crystals in equilibrium with a liquid of composition O, and R is read off the solidus curve for crystals in equilibrium with liquids on the cotectic curve (in this case at P).

(vii)   At P on Figure 25, the crystallizing plagioclase is joined by diopside (of fixed composition, remember). *P is the eutectic point* in the simple eutectic system between diopside and plagioclase of the composition *in the liquid* at P. The composition of the plagioclase in a sample of composition P may be estimated from its position on Figure 25 (e.g. as if you did ITQ 12 in reverse) but the important point is that it is clearly richer in albite than the plagioclase that crystallized first.

(viii)   As indicated earlier, the Di–Ab–An system is really a whole series of binary eutectic systems between diopside and all the plagioclase compositions between pure anorthite and pure albite. Thus, as the temperature falls below that at P (about 1 230 °C, Figure 25), the composition of the plagioclase continues to become richer in albite and we therefore effectively move sideways to another eutectic point in the adjacent binary system of diopside and plagioclase that is slightly richer in albite. The curve on which P and M are situated is made up of a whole series of eutectic points in simple eutectic systems between diopside and a continuum of plagioclase compositions. This curve, which is the line of the trough in the liquidus surface in Figures 23 and 24, is called the *cotectic curve*.

cotectic curve

As the temperature falls below that at P, crystals of plagioclase and diopside form together. The composition of the diopside clearly remains fixed, but that of the

plagioclase continues to become more albite-rich. The composition of the liquid migrates along the cotectic curve towards M. Such crystallization along a cotectic curve is often referred to as *cotectic crystallization*. Moreover, as the liquid moves from P towards M, we can see from the projected liquidus and solidus curves for compositions on the cotectic curve (Figure 24) that the composition of the plagioclase crystals (on the solidus) changes from R to N.

How do we determine the composition of the last drop of liquid to crystallize under equilibrium conditions in the plagioclase feldspar system (Figure 16)?

Crystallization stops (it is complete) when the crystals have the same composition as the bulk sample. The last drop of liquid (point e on Figure 16) is on the liquidus at the same temperature as those crystals.

(ix)   Similarly, under equilibrium conditions in the ternary system Di–Ab–An, crystallization stops when the plagioclase crystals have the same composition as those in the bulk sample (the initial liquid). For our sample in Figures 24 and 25, that occurs when the crystals (on the solidus) are of An_{50}—point N. In this ternary system, those crystals are at 1160 °C, and they must be in equilibrium with the liquid that is on *the cotectic curve at the same temperature*—at point M (1 160 °C on the cotectic curve). Thus, if bulk equilibrium has been maintained during cooling, the last drop of liquid has the composition M; once that has crystallized, the sample has moved from the solid-and-liquid field to the solid-only field.

The solid end product, after equilibrium crystallization, will be an aggregate of diopside and An_{50} plagioclase crystals. Moreover, the bulk composition of the solid end product must of course be the same as that of O, the starting composition.

Finally, one of the properties of Figure 25 is that the *tie-line* between the two minerals that co-exist in the end product (in this case diopside and An_{50}) must intersect the bulk composition O. A pencil line drawn from N to Di must therefore run through the bulk composition O, and if you draw that line on the Figure you can see that it does.

This is the ideal point for you to fix some of these concepts more firmly in your mind by completing AV 05, which deals with ternary phase diagrams, using the Di–Ab–An system as an example. The AV sequence will take you about 45 minutes to complete, and it starts in the AV Notes, to which you should now refer.

ITQ 13   A rock melt consists of 80 per cent Di, 10 per cent Ab, and 10 per cent An. Use Figures 24 and 25 and model 1 (referring back to Figures 13 and 16 if necessary) to predict:

(a)   The temperatures at which crystallization will begin.

(b)   The sequence of mineral phases that form as the liquid cools.

(c)   The composition of the first and the last plagioclase to crystallize from the liquid.

By using the Di–Ab–An system as an example, we have seen how the order in which minerals crystallize can be predicted depending on (i) the composition of the sample (the original melt), and (ii) the form of the experimentally determined phase diagram (for example, Figure 24). In Section 5 we shall consider in more detail how the *chemical composition* of a liquid changes as different minerals crystallize from it.

4.4   Summary of Section 4

(a)   Many minerals do not have fixed compositions, but are part of solid-solution series made up of mixtures between two (and occasionally more) end-member minerals: common examples are the plagioclase series between albite and anorthite and the olivines between forsterite and fayalite.

(b)   As with binary eutectic systems, crystallization (or melting) in such systems takes place over a *range of temperatures*, but in this case the compositions of both the liquid and the crystals change continuously while the total sample is in the solid-and-liquid field. The first crystals are relatively enriched in the high-temperature end-member (for example, anorthite, Figure 16), but both crystals and liquid become richer in the low-temperature end-member (for example, albite, Figure 16) as the temperature falls.

(c)   Such changes in composition take place by continuous *reaction* between the crystals and the liquid. Thus, if equilibrium is to be maintained, there must be sufficient *time* for the ions involved (in both the crystals and the liquid) to move to and from the edges of the crystals (where such reaction takes place).

(d) If bulk equilibrium is not maintained between the crystals and the liquid, the later liquids are relatively *depleted* in the high-temperature end-member and correspondingly *enriched* in the low-temperature end-member.

(e) In general, non-equilibrium crystallization may take place for two reasons: either the temperature falls too rapidly for the inner portions of individual crystals to re-equilibrate with the later, low-temperature liquids (resulting in zoned crystals, for example, the plagioclase feldspar in Figure 18); and/or the crystals and the liquid are simply separated physically—as in fractional crystallization (Figure 4).

(f) Ternary systems consist of three components, or minerals, and variations of composition against temperature may be illustrated either on three-dimensional models (for example, model 1, Di–Ab–An) or (more usually) by projecting liquidus temperature contours onto a triangular diagram. The principles controlling the evolution of both crystals and liquid (particularly while they exist together) are the same as those discussed earlier for the simpler two-component systems.

4.5 Objectives for Section 4

Now that you have completed Section 4, you should be able to:

1 Define in your own words, or recognize valid definitions of, the terms flagged in the margins of this Section.

10 Recognize and explain the significance of the main features on a phase diagram of temperature against composition for a binary system within which there is solid solution between the two end-members.

11 Use such phase diagrams to describe crystallization and melting behaviour of samples made up of mixtures of two components between which there is solid solution.

12 For two-component systems, calculate how much crystallization has taken place when a sample is at a particular temperature—that is, for particular compositions of the crystals and the liquid.

13 Explain in your own words the effects of non-equilibrium crystallization in simple two-component eutectic and solid-solution systems.

14 Plot the composition of a sample consisting of a mixture of three components on a triangular variation diagram.

15 Describe the equilibrium crystallization and melting behaviour of a sample in a ternary system.

Apart from Objective 1, to which they all relate, the five ITQs in this Section test these Objectives as follows: ITQ 9: Objective 11; ITQ 10: Objective 12; ITQ 11: Objective 13; ITQ 12: Objective 14; ITQ 13: Objective 15.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 8 (*Objectives 10 and 11*) In a binary system, the paths taken by the crystals and the liquid during melting are the reverse of those taken during crystallization—assuming that equilibrium is maintained in each case. With reference to Figure 16, answer these questions about what happens to a sample of An_{70} as it is *heated* from 1 200 to 1 600 °C.

(a) Is the sample still completely solid at 1 300 °C? What is the composition of the crystals?

(b) What is the name given to the boundary between the solid-only and the solid-and-liquid fields?

(c) At what temperature does the first liquid appear and what is its composition?

(d) At 1 450 °C, is the sample An_{70} completely solid, completely liquid, or does it contain a mixture of solid and liquid?

(e) What are the compositions of the crystals and the liquid at 1 450 °C?

(f) At what temperature do the last crystals disappear and what was their composition?

(g) At 1 600 °C, is the sample completely liquid, completely solid, or does it contain a mixture of crystals and liquid?

SAQ 9 (*Objective 12*) A sample of Fo_{30} (30 per cent forsterite, 70 per cent fayalite) is cooled from 1 600 °C. At 1 400 °C, how much of the sample has crystallized? (Determine the composition of the crystals and the liquid that co-exist at 1 400 °C from the phase diagram for olivines in Figure 20.)

37

SAQ 10 (*Objective 13*)   Figure 27 illustrates the variation in the forsterite content of olivines at different heights in the Skaergaard intrusion.

(a)   Can you suggest an explanation for the fact that the olivine crystals do not all have the same forsterite content?

(b)   Which olivines crystallized at the higher temperatures?

(c)   Which olivines crystallized first—those higher or lower in the intrusion? Give your reasons.

(d)   Assume for the moment that the system consisted only of a mixture of forsterite and fayalite. Use Figure 20 to estimate the temperature of crystallization of the crystals at 1 000 m in the intrusion.

(e)   In practice, the basic magma contained more components than just forsterite and fayalite. Would you therefore expect that your estimate of temperature in (d) was too high or too low?

SAQ 11 (*Objective 14*)   Plot these two samples on Figure 26.

(i)   30 per cent P, 20 per cent Q, and 50 per cent R.

(ii)   200 g P, 125 g Q, and 175 g R—remember to re-calculate these weights as percentages.

SAQ 12 (*Objective 15*)   A liquid consists of 60 per cent diopside, 30 per cent albite and 10 per cent anorthite. Use Figures 25 (and 26) and model 1 to predict:

(a)   The temperature at which the first crystals appear.

(b)   The composition of those first crystals.

(c)   The temperature at which the second mineral starts to crystallize.

(d)   The path followed by the liquid while the two minerals are crystallizing together.

(e)   Assuming that complete equilibrium is maintained throughout crystallization, what is the composition of the last plagioclase crystals to form before solidification is complete?
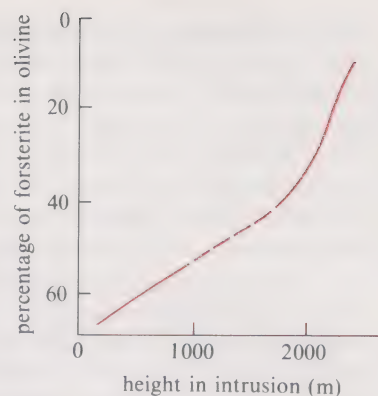

FIGURE 27   The chemical composition of olivine crystals at different heights in the Skaergaard intrusion.

5   Major-element variations

Study comment   We have seen that rocks melt, and crystallize, over a range of temperatures and pressures. The compositions of the liquids change continuously depending on the compositions of the mineral(s) they are in equilibrium with. In Sections 5 and 6 we combine information from phase diagrams (for example, which minerals will crystallize and in what order) with actual chemical analyses on both rocks and minerals to investigate whether the chemical variations observed in particular suites of igneous rocks may be explained by the processes of partial melting and fractional crystallization discussed in previous Sections.

Elements analysed in rocks are commonly termed major, minor and trace elements depending on their abundance. Major and minor element contents are usually reported as oxides and expressed in weight per cent (see Block 1 and Tables 1 and 2 in this Block). Trace elements are by definition present in very small amounts and analyses are usually presented in parts per million (p.p.m.) or even parts per billion (p.p.b.; 10^{-9}). They are discussed in much greater detail in Section 7.

Major elements clearly make up most of a rock (98–99 per cent) and as such they will each provide important lattice-forming ions to at least one of the minerals present. Thus, major-element variations in igneous rocks should be consistent with the minerals that are present and the order in which they crystallized (Block 1, Section 4.1, ITQ 25, Figure 41). In practice, we may study the chemical analyses of a suite of rocks and infer which minerals crystallized and in what order. Then, using experimentally determined phase relations (like those in Figures 13, 16, 20, 25), we may be able to estimate the temperatures and pressures (that is, the depths) at which crystallization took place. As we shall develop in more detail later, this meeting between chemistry and the information portrayed on phase diagrams is the essence of classical igneous petrology.

Let us start by returning to the system Di–Ab–An, which we looked at in Section 4. Consider the liquid that has 14 per cent diopside, 43 per cent albite, and 43 per cent anorthite and that plots at point O in Figure 25. Table 3 contains chemical analyses of the three pure minerals, diopside, albite and anorthite. That enables us to calculate the chemical composition of the sample at point O on Figure 25.

TABLE 3   Chemical analyses of diopside, albite and anorthite. Results expressed in weight per cent

	diopside $CaMgSi_2O_6$	albite $NaAlSi_3O_8$	anorthite $CaAl_2Si_2O_8$
SiO_2	55.5	68.6	43.2
Al_2O_3	—	19.4	36.6
MgO	18.6	—	—
CaO	25.9	—	20.2
Na_2O	—	11.8	—

The SiO_2 content of a sample with 14 per cent diopside, 43 per cent albite, and 43 per cent anorthite may be calculated as follows:

SiO_2 in sample = (SiO_2 in diopside) + (SiO_2 in albite) + (SiO_2 in anorthite)

SiO_2 in diopside = weight per cent of SiO_2 in diopside (55.5) $\times$ proportion of diopside in sample (14/100)

$$= 55.5 \times \frac{14}{100}$$

and similar calculations can be done for SiO_2 in albite and in anorthite.

Therefore,

$$SiO_2 \text{ in sample} = \left(55.5 \times \frac{14}{100}\right) + \left(68.6 \times \frac{43}{100}\right) + \left(43.2 \times \frac{43}{100}\right)$$
$$= \quad 7.77 \quad + \quad 29.5 \quad + \quad 18.6$$
$$= 55.9 \text{ per cent}$$

Similarly, for MgO, which is only present in diopside:

$$MgO \text{ in sample} = \left(18.6 \times \frac{14}{100}\right) + \left(0 \times \frac{43}{100}\right) + \left(0 \times \frac{43}{100}\right)$$
$$= 2.60$$
$$= 2.6 \text{ per cent}$$

ITQ 14   Using the method outlined above for SiO_2 and MgO, calculate the Al_2O_3 and Na_2O, contents of a liquid with 14 per cent diopside, 43 per cent albite, and 43 per cent anorthite. Write your results in the spaces provided in Table 4.

TABLE 4   Calculated compositions of liquids at positions O, P and M in Figure 25—the Di–Ab–An system. Oxides expressed as weight per cent

	O	P	M
SiO_2	55.9	59.3 .	64.6
Al_2O_3	*	18.1	18.4
MgO	2.6	5.1	2.4
CaO	12.3	11.6	5.2
Na_2O	*	5.9	9.2

* Fill in from ITQ 14.

When you have filled in the two missing items in the 'O' column, Table 4 should contain the compositions of the liquids at points O, P and M in Figure 25; that is, at different stages during the crystallization of plagioclase and diopside. They illustrate how, for example, SiO_2 and Na_2O increase, but CaO decreases from O, via P, to M. However, such variations in composition are much easier to see if plotted graphically on chemical variation diagrams. These are used widely in the study of igneous rocks and are introduced in the next Section.

5.1 Chemical variation diagrams

Chemical variation diagrams are simply diagrams on which chemical variations may be usefully represented. The choice of what to plot rests with the geochemist and what he or she wishes to communicate or explore. For major elements in igneous rocks one of the most popular techniques is to plot various elements (or more usually their oxides) against SiO_2. It is then possible to assess the data visually and to begin to interpret them in terms of some combination of partial melting and fractional crystallization. In this discussion we shall concentrate primarily on fractional crystallization.

The variations of MgO, CaO and Na_2O in the liquids O, P and M (Table 4) have been plotted against SiO_2 in Figure 28. It is easy to confirm that CaO decreases from O through to M, as we concluded from looking at Table 4. However, what is more striking and very much harder to ascertain by simply looking at a list of analyses, is that for each of these particular oxides the *slope* on the variation diagram is different between O and P from that between P and M. The extreme example is MgO, which increases from O to P and then decreases from P to M. Such changes in slope result in 'kinks' in the trends on the chemical variation diagrams which are very important when it comes to interpreting such trends in terms of the different minerals that may be crystallizing or melting.

We shall therefore look briefly at the general properties of such element versus element variation diagrams, and this is most easily done through what are called *mixing calculations*. These enable us, for example, to calculate graphically the way the liquid composition changes as a particular mineral separates from it. When we have examined the principles of these calculations we shall come back and apply them to Figure 28.

5.2 Simple mixing calculations

Figure 29 is a chemical variation diagram and X and Y are any two elements (or oxides) whose concentrations are expressed by weight; for example, weight per cent or parts per million. On such a diagram, if composition R is added to composition S, then the resultant mixture (T) lies somewhere on the *straight line* R–S. Moreover, since in this example the mixture T is nearer to R, it must contain more of R than of S.

Apart from the fact that we are now discussing weights (of oxides, for example) rather than volumes of crystals and liquid, the principles involved in the mixing calculations are exactly the same as those used in our earlier calculations of how much plagioclase had crystallized from a melt (Figures 16 and 17). The relative amounts of R and S in mixture T in Figure 29 are proportional to the distances ST and TR respectively. Thus the proportions of R and S are given by:

$$\frac{\text{weight of R}}{\text{weight of S}} = \frac{ST}{TR}$$

where ST and TR are distances measured in Figure 29. The percentage amounts of the end members R and S are:

$$\text{weight per cent of R} = \frac{100\,ST}{SR}$$

$$\text{weight per cent of S} = \frac{100\,TR}{SR}$$

It is very important to note that this relationship applies *only* to diagrams of one element (or oxide) against another (for example, MgO versus SiO_2): it does *not* apply to diagrams where the *ratio* of two elements is plotted against one element or another element ratio.

But how does the mixing of two materials (e.g. R and S) help us to understand what happens during, for example, fractional crystallization?

During fractional crystallization, crystals form and are removed from the liquid. If you like, the original sample becomes *unmixed*! Look at Figure 30. If a mineral plotting at A crystallizes from an initial liquid B, the *residual liquid* will evolve towards L (Figure 30). Since the composition of B may then be expressed as a
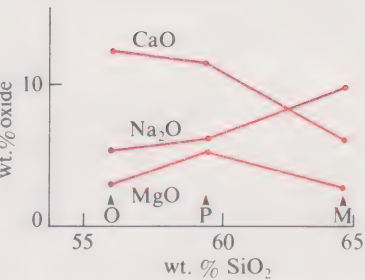
FIGURE 28   Variations of MgO, CaO and Na_2O against SiO_2 in the diopside–albite–anorthite system for liquids O, P and M in Figure 25.
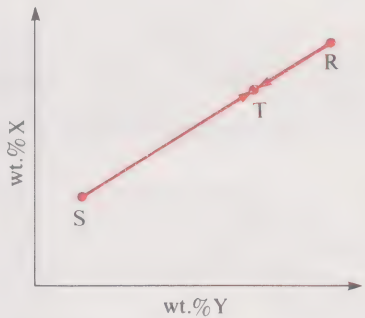
FIGURE 29   Chemical variation diagram illustrating mixing between two substances R and S composed of different amounts of X and Y.
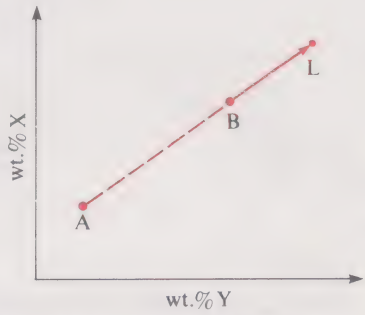

FIGURE 30   Chemical variation diagram illustrating that crystallization of mineral A from liquid B drives the composition of the liquid towards L.

40

mixture of the crystals that have crystallized (at A) and the residual liquid (for example, at L), then A–B–L must be a straight line and we can apply the equations outlined above for mixing between two components (Figure 29).

Thus the amount of mineral A that needs to crystallize for the composition of the liquid to evolve from B to L (Figure 30) is given by

$$\text{weight per cent of A} = \frac{100\,\text{BL}}{\text{AL}}$$

There is also a relationship between the distance the liquid has evolved along the line BL, the distance between the composition of the crystals and the composition of the original sample (AB), and the *quantity* of crystals formed. If the crystals are very different in composition from the original liquid, the formation of a small quantity of crystals causes a relatively large change in the composition of the residual liquid. Conversely, if the crystals and the original liquid have similar compositions, a large amount of crystallization is needed before it has much effect on the composition of the residual liquid.

> **ITQ 15** Using a metric ruler, measure the distances AB, AL and BL on Figure 30.
>
> (a) How much crystallization of mineral A is needed to drive the composition of the liquid from B to L?
>
> (b) How much crystallization of A would be needed to move the liquid from B to L, if the composition of A was much closer to that of the original liquid B so that the distance A–B was only 10 mm?
>
> Express your answers in weight per cent.

A feature of such calculations is that the composition of the material being removed (A in Figure 30) need not be that of a *single* mineral. It might easily be the composition of two or more minerals that crystallize together, as, for example, when a liquid is moving down a cotectic curve such as that in Figure 24. Thus the material that is being removed from the liquid and that consequently 'controls' its evolution, is usually referred to as the *extract*. In Figure 31a A′ is the composition of the extract, but in this example it does not correspond to the composition of a single mineral but rather to that of a mixture of two minerals C and D.

extract (mineral extract)

> How could you calculate the proportions of minerals C and D that are present in the extract A′?

In exactly the same way as we calculated the proportions of R and S that were present in the composition of the mixture T in Figure 29. Thus (remembering that A′ lies nearer to D than to C, so there must be *more* of D):

$$\frac{\text{weight of C}}{\text{weight of D}} = \frac{\text{A}′\text{D}}{\text{A}′\text{C}}$$

and if in Figure 31a, A′C = 2 units and A′D = 1 unit, then

$$\frac{\text{weight of C}}{\text{weight of D}} = \frac{1}{2}$$

Therefore, as the ratio (by weight) of mineral C to mineral D is $\frac{1}{2}$, we may conclude that the extract A′ contains twice as much of mineral D as it does of mineral C.

Finally, Figure 31b illustrates an example of what may occur if *three* minerals crystallize together. Extract A″, which controls the evolution of the liquid from M to N, consists of minerals H, G, and I, and it therefore plots within the triangle HGI. Its position in that triangle depends on the proportions of H, G and I in A″, in the same way that in Figure 26 the position of Z depended on the proportions of P, R and Q.

Note that in Figures 31a and 31b the position of the extract (A′ and A″) will change if the *proportions* of the crystallizing minerals in the extract change. As suggested by the crystallization paths we have discussed in two- and three-component systems (Ab–An, Di–Ab–An, and so on), such changes are likely to be commonplace in natural rock systems.

These are the basic principles of mixing calculations as applied to arguments about the evolution of liquid compositions on simple variation diagrams. We should now be able to apply them to a couple of examples.

(a)

(b)

FIGURE 31 Chemical variation diagrams illustrating how liquids change in composition when (a) two, and (b) three, minerals crystallize together.

5.3 Geochemical variations in the diopside–albite–anorthite system

The calculated CaO, MgO and SiO$_2$ contents of liquids O, P and M in the system Di–Ab–An (Figure 25 and Table 4) have been replotted on larger diagrams (Figures 32a and 32b) so that there is also room to plot the compositions of the minerals present, diopside and plagioclase. The diopside composition is fixed and is taken from Table 3. However, as we discussed earlier, the composition of plagioclase changes as the temperature falls and the composition of the liquid changes. Since plotting this variation in plagioclase would obscure more important aspects of Figure 32, we have approximated the real situation by plotting a plagioclase feldspar of intermediate composition—about An$_{65}$ (35 per cent albite, 65 per cent anorthite) containing CaO = 13 per cent, MgO = 0 per cent, SiO$_2$ = 52.3 per cent.
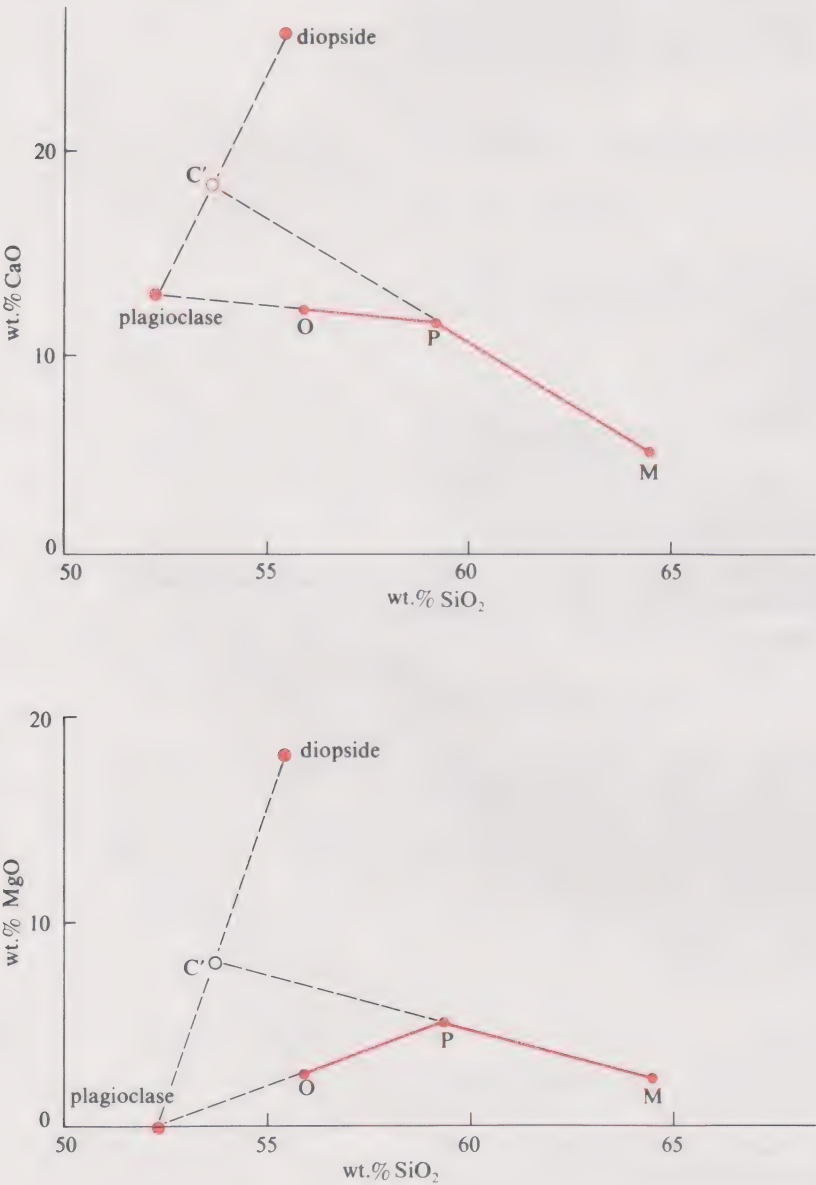
FIGURE 32   Variations of oxides in liquids and crystals from the diopside–albite–anorthite system: (a) CaO against SiO$_2$; (b) MgO against SiO$_2$.

> Consider the evolution of liquid O to liquid P. Remember that the original liquid (in this case O), the resultant liquid (P), and the composition of the crystals extracted should lie on the same straight line in Figure 32. Which mineral has to be removed to control the evolution from O to P? Do you get the same answer using both MgO and CaO (Figures 32a and 32b)?

The answer is clearly plagioclase, since O, P and the plagioclase composition lie on straight lines on both graphs.

Using MgO as an example, we might express this mineral control another way. Since the plagioclase has no MgO, it obviously has less MgO than the liquid. Removal of plagioclase must therefore increase the MgO content of the liquid, and this is what is observed as O evolves to P in Figure 32b.

We may also calculate *how much* plagioclase (of average composition An_{65}) has crystallized while the liquid evolves from O to P, using the equations presented for Figures 29 and 30:

$$\text{weight per cent of plagioclase} = \frac{100 \times OP}{\text{plagioclase} - P}$$

$$= \frac{100 \times 19}{38} \text{ (from Figure 32a)}$$

$$= 50$$

That is, 50 per cent of sample O must crystallize as plagioclase of average composition An_{65}, for the liquid to evolve from O to P. Moreover, although this calculation was done for CaO versus SiO_2, you get the same result using MgO versus SiO_2 (Figure 32b). Try that for yourself and see if you also arrive at this conclusion!

> Variations of CaO, MgO and Na_2O with SiO_2 (Figures 28 and 32) all exhibit a pronounced 'kink' at the composition of P, that is, in all cases the slope of OP is different from that of PM. What does this 'kink' signify?

The first point to strike you should be that while OP was apparently controlled by the separation of plagioclase only, this cannot possibly be true of PM—the composition of plagioclase does not plot on the extension of the line PM in either of the variation diagrams in Figure 32. Thus a kink in the chemical trends on such diagrams signifies a *sharp change* in what is controlling the evolution of the liquid. It implies either that a particular mineral is no longer crystallizing or that a new one has just started to crystallize.

In our example, the lines PM for the different elements point back to a composition C′, which consists of a mixture of plagioclase and diopside. Extraction of C′ would therefore drive the liquid from P to M, and we may conclude that diopside started to crystallize when the melt had composition P, and that plagioclase continued to crystallize along with the diopside.

In summary, we have been able to deduce, by looking at the chemical variations in different liquids, that from O to P only plagioclase was crystallizing, while the evolution from P to M was controlled by the crystallization of *both* plagioclase and diopside. We have also seen that, theoretically at least, we may estimate the amount of crystallization from both phase diagrams and chemical variation diagrams and see how they compare; although, in practice, this is often complicated by the changing composition of minerals like plagioclase for which it was necessary to assume an average composition in Figure 32. Nonetheless, the sequence of crystallization inferred for the Di–Ab–An system from Figure 32 is the same as that deduced earlier from the phase diagram (Figure 25).

For such a relatively simple experimental system this conclusion is not in itself surprising; however, in more complex systems, which are a better representation of natural rocks, the minerals and the order in which they crystallize often vary with *pressure* as well as with temperature and composition. The power of the technique is that if we can deduce the order in which minerals crystallized using the chemical variations in a suite of igneous rocks, we should be able to infer (from experimentally determined phase relations) the conditions of pressure and temperature that prevailed during the generation and evolution of the magmas.

There is one extremely important point which has so far received little attention and which must now be considered before taking our leave of the Di–Ab–An system. *Throughout this discussion we have assumed that there was equilibrium between the crystals and the liquid, and that implies that they remained in contact with each other*— although they obviously plot in different places on both phase diagrams and chemical variation diagrams. As depicted in Figure 4 (p. 10), we have been discussing *crystallization*, but not *fractional crystallization*. But what happens to the composition of the liquid in the Di–Ab–An system if early formed crystals are separated physically from the liquid and bulk equilibrium is not maintained?

Make sure you remember the effect of equilibrium and non-equilibrium in simple eutectic and solid-solution systems (Section 4.2) by answering ITQ 16.

ITQ 16 (a) In a binary eutectic system such as Di–An (Figure 13, p. 21) is the composition of the liquid at any particular temperature different during non-equilibrium crystallization from its composition during equilibrium crystallization?

(b) In the plagioclase system (Figures 16 and 19), will residual liquids produced by non-equilibrium crystallization (i) have the same composition, (ii) be richer in albite, or (iii) be richer in anorthite, compared with those produced under equilibrium conditions?

Your answer to part (b) of ITQ 16 is most relevant to this discussion. Under equilibrium conditions, the last drop of liquid remaining from our original sample with 14 per cent Di, 43 per cent Ab and 43 per cent An (point O) plotted at point M in Figure 25. That was the composition of the liquid in equilibrium with plagioclase crystals similar in composition to that of the feldspar in the original sample An_{50}—composition N on the Ab–An solidus for liquids on the cotectic curve (Figure 24 and model 1).

However, under non-equilibrium conditions, the early-formed plagioclase crystals no longer re-equilibrate with the later, lower-temperature liquids; therefore

(i) the liquid becomes richer in albite (Figure 19);

(ii) it persists to lower temperatures (Figures 16, 19);

(iii) it evolves further down the cotectic curve (on the low-temperature side of M, Figure 25).

We may conclude that *non-equilibrium crystallization in the ternary system Di–An–Ab drives the residual liquid further down the cotectic trough*, and under extreme conditions it may even reach the Di–Ab eutectic point. Such a liquid clearly contains no anorthite and from Figure 25 we can see that it contains well over 90 per cent albite.

Look at Tables 3 and 4 (p. 39). Can you assess whether this liquid at the Di–Ab eutectic (less than 10 per cent Di, over 90 per cent Ab, no An) contains more or less SiO_2 and CaO, for example, than liquid M (Figure 32a)?

The Di–Ab eutectic liquid should have more SiO_2 and less CaO than liquid M (Table 4). In fact, the composition of the Di–Ab eutectic liquid (calculated by the same method used to compile Table 4) has MgO = 0.7 per cent, CaO = 1.0 per cent, and SiO_2 = 68.2 per cent. If you plot these results on Figure 32 you will see that they lie roughly on the continuations of the trends P–M on the two diagrams.

Thus we arrive at a conclusion that is extremely important when we come to consider the chemical variations found in igneous rocks. Fractional crystallization (that is, isolation of the early formed crystals from the liquid) in the system Di–Ab–An can result in a suite of liquids with a wide range of chemical compositions, for example, SiO_2 varies from 56 to 68 per cent, and CaO from 12 to 1 per cent. Let us see how these variations compare with those observed in natural rocks!

5.4 Igneous processes beneath two island-arc volcanoes

Processes along constructive and destructive plate margins result in two different, but very common igneous rocks.

From Block 1, can you remember what they are?

Basalt is produced in large quantities in the formation of ocean crust at constructive plate margins, whereas *andesite*[A] appears to be the dominant extrusive rock type along destructive plate margins. Basalt is generated by partial melting of peridotite, but andesite may be produced both within and above the subducted slab of oceanic lithosphere (Block 1, Section 4.1).

Can you remember what different rock types occur within and above the subducted ocean crust at the depths where magma is generated? (Look back at Block 1, Figure 42, if you are not sure.)

The subducted ocean crust consists predominantly of ocean-ridge basalts (and gabbros) which have probably been metamorphosed to form *eclogite*[A]. However, eclogites usually have major-element compositions similar to those of the original basalts. So *partial* melting of eclogite will not produce basalt. Rather, the partial melt would be dominated by the lower-temperature components in eclogite and it would have the composition of andesite. This contrasts with liquids produced from above the descending slab. The material there is peridotite and, as we discussed in Section 1 of this Block, partial melting of peridotite generates basalt, not andesite.

In summary, therefore, partial melting *within* the descending slab should produce magmas of intermediate compositions, whereas melting *above* it should produce basic, or basaltic, magmas. However, there is a complication—andesite can also result from fractional crystallization of basaltic liquid!

So, we must modify our approach to understanding where andesites come from. By studying andesites in an area where there is a variety of rock types that might be related to them, we may assess whether fractional crystallization has taken place and what effects it may have had. Only then is it possible to estimate the composition of the original liquid and, thus, whether its *source* rock was likely to have been subducted ocean-floor basalt or upper-mantle peridotite.

The concept of an original or initial liquid is very important in geology. Such liquids are often called '*primary*' *melts* or *liquids* and they carry the clear implication that they represent an estimate of the composition of the liquid *when it left the zone of partial melting* (see Figure 2), before it started to change its composition perhaps by fractional crystallization or by contamination with other material *en route* to the surface.

primary melt or liquid

The eastern islands of the Caribbean (Figure 33) are a very good example of an *island-arc*[A] system: they are mainly volcanic and were formed by igneous processes above a subduction zone. Volcanoes on some of the islands are still active (for example, Mt Soufrière on St Vincent erupted in 1979) and the need to understand volcanic processes, and particularly the risks to neighbouring population centres, has been at least in part responsible for the considerable amount of work that has been done in this area. As our example we have chosen two volcanoes on the island of Dominica, which were the subject of a detailed study by Dr K. J. A. Wills while he
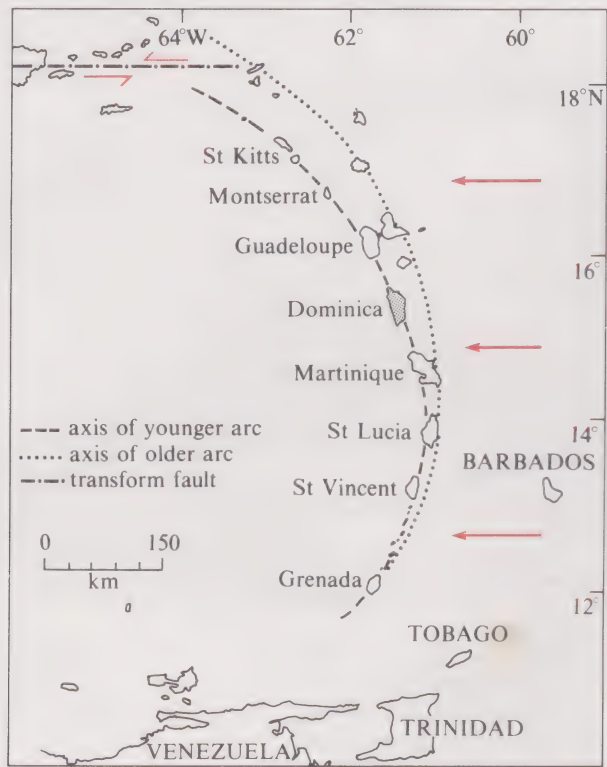

FIGURE 33 Sketch map of the Lesser Antilles island-arc system in the eastern Caribbean. All recent volcanic activity has taken place along the axis of the younger arc. The arrows represent the relative movement of the Atlantic ocean crust presently being subducted under this island-arc system.

was a student at the University of Durham. Both these volcanoes have been active in the last few million years, but while one erupted predominantly basaltic lavas the other appears to have produced andesites and rocks of higher SiO_2 contents. The two volcanoes are quite close to one another and by studying them it was hoped to ascertain whether the basalts and the andesites were related to one another and thus whether they could have been derived (by fractional crystallization) from the same *primary liquid*.

Figure 34 is a plot of CaO against SiO_2 and Figure 35 shows MgO against SiO_2 for selected lavas from the two volcanoes. It is very striking how in both diagrams the data plot on reasonably smooth curves. In all previous discussions of both phase diagrams and chemical variation diagrams we have talked in terms of *crystals* and *liquids*. But what about *rocks*? What do they represent if we analyse them and plot their compositions on diagrams like Figures 34 and 35?
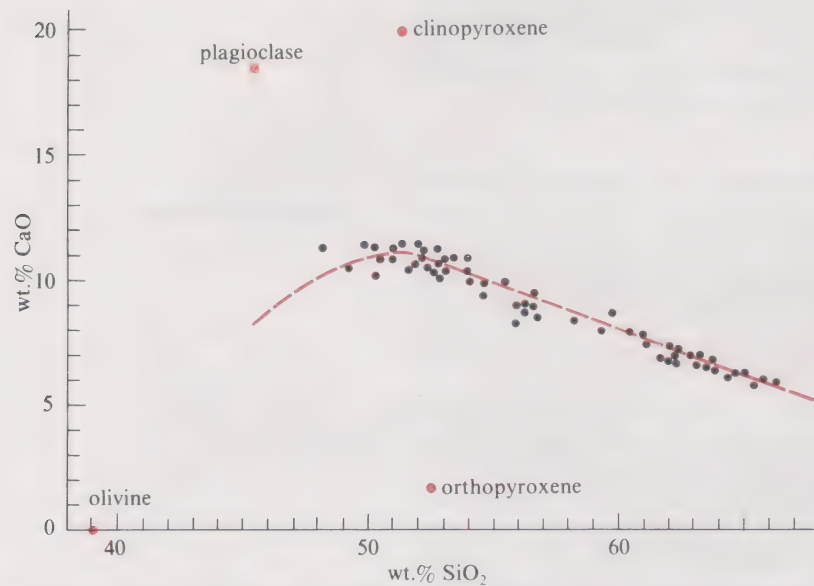
FIGURE 34   Variations of CaO and SiO_2 in a suite of lavas and phenocryst minerals from two volcanoes on the island of Dominica.
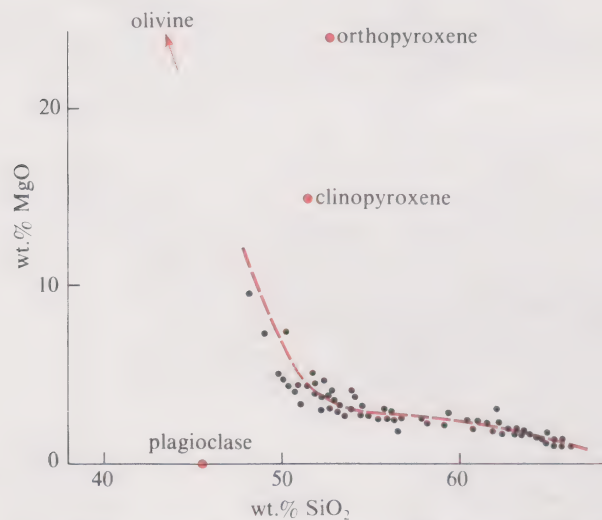
FIGURE 35   Variations of MgO and SiO_2 in a suite of lavas and phenocryst minerals from two volcanoes on the island of Dominica.

The answer will inevitably depend on the particular rock, but what we must be looking for are examples which (on the basis of texture) we believe to represent *crystals* and *liquids*. Crystals are comparatively easy: either they occur as phenocrysts (as in Figures 3b and 14, for example) or they have become separated from the liquids and collected together in rocks called *cumulates*[A]. Cumulates are crystalline rocks that came together *after the crystals formed* and although they presumably form at depth where fractional crystallization is in progress, lumps of cumulates are sometimes brought up to the surface during subsequent eruptions.

Selecting rocks that you confidently believe to represent samples of liquid is very much more difficult, but since most discussions of major-, minor- and trace-element geochemistry centre on reactions between crystals and liquids, it is clearly extremely important. The simplest solution is to look for very fine-grained rocks that contain no phenocrysts (for example, Figure 3a) since that suggests they cooled too rapidly for early crystals to form and separate from the liquid. However, it is unusual for rocks with more than 50 per cent SiO_2 to be fine-grained (and they often have phenocrysts) and then you have to look for *textural* and *chemical* evidence that the various crystals and the groundmass (liquid) are in equilibrium with one another.

Chemical evidence relies on the fact that we may predict, from the study of phase relations, the composition of the liquid in equilibrium with a particular mineral—or combination of minerals. For example, we argued that in the Di–Ab–An system (Figure 25) liquid of composition M was in equilibrium with plagioclase crystals of An_{50} and diopside. Thus if a sample has a liquid of composition M co-existing with plagioclase of An_{80}, it suggests that they are *not* in equilibrium. In other instances, disequilibrium may be even more obvious—as when minerals co-exist with liquids from which they could never have crystallized, for example, K-feldspar in an ultrabasic liquid, or olivine in a granitic liquid. The bulk composition of such samples will reflect their unrelated constituents and thus they cannot represent liquid compositions.

Figure 36 illustrates several textures you might observe in a suite of volcanic rocks. Answer ITQ 17 to make sure that you know which are most likely to represent liquid compositions.
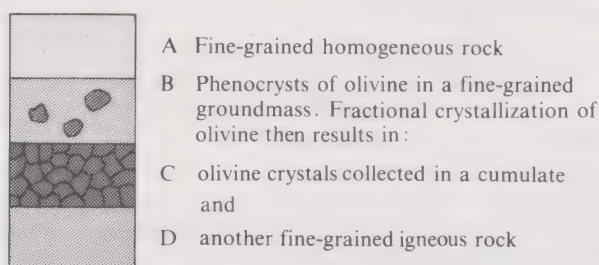

A Fine-grained homogeneous rock

B Phenocrysts of olivine in a fine-grained groundmass. Fractional crystallization of olivine then results in:

C olivine crystals collected in a cumulate and

D another fine-grained igneous rock

FIGURE 36   Schematic descriptions of the textures in four volcanic rocks, for use with ITQ 17.

> **ITQ 17**   Each of the four boxes in Figure 36 is a sketch of the texture (that is, the relationship between crystals) in a rock that has been crushed up, well mixed to form a homogeneous powder, and then analysed. You may assume that phenocrysts are in equilibrium with the co-existing groundmass. From the descriptions of the textures, which powder(s) are most likely to represent (i) crystals, and (ii) liquids?

Returning to the volcanic rocks from Dominica, the samples selected for analysis and plotted in Figures 34 and 35 are those thought to represent liquids. *If* that is correct and *if* these liquids can be shown to be related (for example by fractional crystallization), then the smooth trend of results on such chemical variation diagrams represents the *path* taken by the evolving liquid. It may therefore be compared directly with the liquid evolution paths discussed in diagrams such as Figures 30–32.

First, however, it is useful to compare briefly the compositions of the Dominica rocks with the calculated compositions of the liquids we have been discussing in the synthetic system Di–Ab–An. The liquids in the Di–Ab–An system varied from 56 to 68 per cent SiO_2 (Figure 32) which is similar to the higher SiO_2 rocks on Dominica (Figures 34 and 35). Over that range of SiO_2, CaO decreases in both the synthetic systems and in the rocks, but the variation of MgO in the former (Figure 32) is significantly different from that in the Dominica rocks. That is, experiments in the Di–Ab–An system reproduced the variations between CaO and SiO_2 in the natural rocks very much better than those between MgO and SiO_2.

> Remembering what elements are present in diopside and plagioclase feldspar, can you suggest why that might be?

The system Di–Ab–An includes the two most common calcium-bearing minerals found in igneous rocks (diopside and anorthite), but it does not contain either of the Mg-rich minerals *olivine* or *orthopyroxene* (orthopyroxene is defined on the next page). Thus it follows that experiments with Di, Ab and An will reproduce variations

of calcium in natural rocks more faithfully than variations of magnesium. Such a conclusion is not intended to criticize the purpose of the experiments, which was to understand relations between those three minerals before proceeding to experiments on more complicated systems which would better reproduce the variations in natural rocks. There is not space to consider these more complicated systems in this Course, but some are discussed in higher-level Earth science Courses.

> Let us look now in more detail at the results from the volcanic rocks on Dominica (Figures 34 and 35). What do you see? Are there any 'kinks' on these variation diagrams?

Yes, there appears to be a kink in the trends at about 50–52 per cent SiO_2 on both diagrams.

> If the observed variations in SiO_2, CaO and MgO were controlled by fractional crystallization, what could you say about the composition of the crystals extracted (the *extract*) compared with that of the liquid? For samples with less than 50 per cent SiO_2, would the extract contain more or less of the following constituents than the liquid: (a) SiO_2, (b) CaO, (c) MgO?

The trends of the data in the rocks with less than 50 per cent SiO_2 (Figures 34 and 35) show an increase in CaO and SiO_2 and a decrease in MgO. The extract must therefore contain (a) less SiO_2, (b) less CaO, and (c) more MgO, than these liquids.

> What about the extract controlling liquids with 55–65 per cent SiO_2?

The extract contains less SiO_2, but more CaO and just slightly more MgO than those liquids.

Analyses of minerals that are commonly found as phenocrysts in the Dominica lavas are presented in Table 5. Their CaO and SiO_2 contents are plotted on Figure 34, and their MgO and SiO_2 contents are on Figure 35. Remember that *clinopyroxene* and *orthopyroxene* are the names given to those members of the pyroxene mineral group that respectively contain a lot (12–22 per cent) and a little (0–2.5 per cent) CaO (Block 1). Ca^{2+} replaces Fe^{2+} and Mg^{2+} within the solid-solution series between $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$. In general, orthopyroxene tends to be a higher-temperature mineral than clinopyroxene; it melts less readily and is thus more common in upper mantle rocks (as you have seen in Block 2).

clinopyroxenes   **orthopyroxenes**

TABLE 5   Analyses of minerals from Dominica (weight per cent)

	plagioclase	clinopyroxene	orthopyroxene	olivine
SiO_2	45.3	51.1	52.4	38.8
Al_2O_3	33.9	1.97	1.63	–
FeO	0.6	10.7	19.3	18.4
MgO	–	14.9	24.0	42.1
CaO	18.4	19.9	1.68	–

Using these analyses we may now evaluate the extent to which *fractional crystallization* could have been responsible for the chemical variations observed in the Dominica volcanic rocks (Figures 34 and 35).

> Look at the trend of the rocks with less than 50 per cent SiO_2 in Figure 34. Does any one mineral plot on the extension of that trend in such a way that crystallization of that mineral will drive the composition of the liquid along that trend?

The dashed line in Figure 34 through these rocks with less than 50 per cent SiO_2 points back towards the composition of olivine (0 per cent CaO, 39 per cent SiO_2). Thus removal of olivine would drive the composition of the liquids up that line until it starts to flatten out at about 50 per cent SiO_2. Similarly, olivine contains abundant MgO and hence removal of olivine drastically reduces the MgO contents of the liquids with less than 50 per cent SiO_2 (Figure 35).

> Look again at Figure 34. What about the rocks with more than 52 per cent SiO_2—could their compositions reflect fractional crystallization of any one of the minerals in Table 5?

The answer must be no. No one mineral plots on line with the trend of the analyses of rocks with more than 52 per cent SiO_2. Thus, if this trend does reflect fractional crystallization, it must be due to the crystallization and removal of more than one mineral. We can see from Figure 34 that some combination of high-calcium minerals (plagioclase and/or clinopyroxene) and low-calcium minerals (olivine and/or orthopyroxene) is required, but how can we find out which of these minerals actually did crystallize together beneath Dominica?

The answer lies in the rocks themselves. Phenocrysts represent minerals that were crystallizing before the liquid was cooled rapidly by extrusion on the Earth's surface. Thus identification of the phenocryst minerals, and their proportions, provides us with an estimate of the bulk composition of the aggregate of minerals that were crystallizing together before they were erupted. We may then use this bulk composition to see if it could control the chemical variation observed in the lavas.

A typical basalt from Dominica has three phenocryst minerals: olivine (10.5 per cent), plagioclase (27.3 per cent) and clinopyroxene (6.2 per cent). These abundances are expressed as percentages of the *total* rock, but they may also be expressed as percentages of the phenocryst assemblage, which therefore consists of 24 per cent olivine, 62 per cent plagioclase and 14 per cent clinopyroxene. On a variation diagram such as CaO against SiO_2, these three minerals form the corners of a triangle, and we may calculate the composition (in this case CaO and SiO_2) of the aggregate phenocryst assemblage using the same method as for ITQ 12 (see also Figures 26 and 31).

> **ITQ 18**   The aggregate phenocryst assemblage (24 per cent olivine, 62 per cent plagioclase and 14 per cent clinopyroxene) contains 14.2 per cent CaO and 44.5 per cent SiO_2. Plot that composition on Figure 34 and see where it plots in relation to the trend of the volcanic rocks with just 52–58 per cent SiO_2. Could fractional crystallization of this phenocryst assemblage be responsible for the variations in CaO and SiO_2 in the lavas with 52–58 per cent SiO_2?

The conclusion from ITQ 18 is that the trend of the chemical compositions of rocks with 52–58 per cent SiO_2 can be produced by fractional crystallization of the minerals which, on textural evidence, are known to have crystallized from Dominica basalts. Moreover, since the CaO and SiO_2 contents of the extract given in ITQ 18 lies on the trend of the lavas up to 66 per cent SiO_2, we might argue that separation of these minerals was responsible for the composition of even the SiO_2-rich rocks. However, in so doing we would be falling into the trap of relying too heavily on the geometric constraints of diagrams such as Figures 34 (and 35) and would be guilty of starting to forget what we know about the rocks themselves.

The phenocryst assemblage used in ITQ 18 was observed in a basalt and *it is therefore not going to occur in rocks of significantly higher SiO_2 contents*. High-SiO_2 rocks like rhyolites largely consist of different minerals (quartz and feldspars) from basalts (olivine, pyroxene and plagioclase feldspar) (Block 1, Figure 41). More specifically, we also know from our own deliberations that the composition of plagioclase feldspar, for example, will change as the composition of the liquid changes: as more crystals form, both the liquid and the crystals become poorer in anorthite (see Figures 16 and 25), that is, poorer in CaO. Thus analyses of plagioclase feldspars in two rocks of higher SiO_2 contents on Dominica give 14.1 per cent CaO, 50.9 per cent SiO_2, and 8.2 per cent CaO, 58.6 per cent SiO_2. If you plot these on Figure 34, you will find that the second analysis actually plots on the trend of the rock analyses which suggests that separation of plagioclase alone could control the compositions of the rocks with the highest SiO_2 content.

A second example is provided by olivine, which is abundant in low SiO_2 rocks, but on Dominica is very rarely observed in rocks with more than 58 per cent SiO_2—the liquids have moved out of the *stability field*^{A} of olivine. Instead, orthopyroxene starts to crystallize and, since like olivine it contains little CaO and significant amounts of MgO, the transition from olivine to orthopyroxene is not marked by any sharp 'kink' on the trends on Figures 34 and 35. Check for yourself where orthopyroxene plots on Figure 34.

In summary, the gradual changes in the chemistry of the lavas from these two volcanoes on Dominica suggest that they may well be related to one another. Moreover, by identifying and analysing the phenocryst minerals we have deduced a fractional crystallization path capable of generating the chemical variations observed in the lavas. That is:

1   At less than 50 per cent SiO_2, olivine crystallizes alone.

2   At 50–58 per cent SiO_2, plagioclase and clinopyroxene crystallize while the amounts of olivine and orthopyroxene decrease and increase respectively.

3   At more than 58 per cent SiO_2, the amount of pyroxene crystallizing becomes less and less until the chemical variation in very SiO_2-rich liquids appears to be controlled by crystallization of plagioclase alone.

Thus we may conclude that the andesites on Dominica appear to have been derived by fractional crystallization from basaltic magma, which, as we argued at the beginning of this Section, itself reflects partial melting of upper mantle peridotite. At least in this example andesite appears to have been derived from *above* rather than *within* the subducted ocean crust. We have also seen how it was possible to argue from experiments on the crystallization of plagioclase that its role as a crystallizing phase became increasingly important in the more SiO_2-rich liquids. Results of experiments on the stability of plagioclase under different *pressures* also reveal that it only occurs as a crystallizing phase at depths of less than 30–35 km. Thus, since the crust beneath Dominica is approximately 30 km thick, we may also conclude that the fractional crystallization we have been discussing took place when the magmas had moved out of the upper mantle and up into the crust (to depths of less than 30 km).

Finally, there is the problem of *how much* fractional crystallization is required.

> **ITQ 19**   (a)   Using the mixing calculation (Section 5.2) and the results on Figure 34, can you estimate how much of an extract 14.2 per cent CaO, 44.5 per cent SiO_2 must be removed from a liquid of 50 per cent SiO_2 to produce a liquid with 66 per cent SiO_2?
>
> (b)   However, we have just argued that the SiO_2 content of the plagioclase, and thus of the extract, increases in more SiO_2-rich liquids. If you take this effect into account, would you expect the amount of fractional crystallization required to change the composition of the liquid from 50 to 66 per cent SiO_2 to be higher or lower than your answer to (a)?

5.5   Summary of Section 5

The minerals in an igneous rock reflect its major-element composition and the pressure and temperature at which it crystallized. As a magma crystallizes, the formation of crystals changes the composition of the *liquid*, while *removal* of such early-formed crystals leaves us with a *sample* of a different composition (that is, fractional crystallization has taken place). Thus removal of crystals from successive liquids results in a suite of liquids of different compositions, and those variations in major-element chemistry reflect the amount and the composition of the mineral(s) that have been removed. In practice, we select samples of igneous rocks which we believe represent liquids. By plotting their compositions on chemical variation diagrams, together with those of the early-formed crystals (now seen as *phenocrysts* or collected together in *cumulates*), we can assess (using mixing calculations) whether fractional crystallization of the observed minerals could have been responsible for the chemical variations seen in the rocks. If the answer is yes, then we may estimate at least the approximate composition of the original liquid and from that it may be possible to infer the composition of its source rock. Applying such arguments to volcanic rocks on Dominica, we have suggested that the andesites and the higher-SiO_2 rocks were derived by fractional crystallization of a basaltic liquid. Since basalt is in its turn derived by partial melting of upper mantle peridotite, we concluded that, at least in this case, the andesites were not obtained by melting subducted ocean-floor basalt, but appear to have been derived from partial melts of peridotite overlying the subducted ocean crust (see discussion in Block 1 and Figure 42, p. 72).

5.6   Objectives for Section 5

Now that you have completed Section 5, you should be able to:

1   Define in your own words, or recognize valid definitions of, the terms flagged in the margins of this Section.

16   Calculate the composition of a sample from the relative proportions of its minerals and their analyses.

17   Use mixing calculations to estimate the amount of fractional crystallization required to change the composition of a liquid by a particular amount.

18   Understand the consequences of non-equilibrium crystallization in a ternary system such as Di–Ab–An.

19   Describe, using chemical variation diagrams, the relationship between crystallizing minerals and the evolution of a liquid.

20   Plot the compositions of a suite of igneous rocks (and of their phenocryst minerals) on a variation diagram and assess whether the individual rocks could be related to one another by fractional crystallization.

Apart from Objective 1, to which they all relate, the five ITQs in this Section test these Objectives as follows: ITQ 14: Objective 16; ITQ 15: Objective 17; ITQ 16: Objective 18; ITQ 17: Objective 19; ITQ 18: Objectives 19 and 20.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 13 (*Objective 18*)   The following questions are about the effects of non-equilibrium crystallization in the Di–Ab–An system (Figures 24 and 25).

(a)   Does non-equilibrium crystallization of diopside and plagioclase drive the liquid along the cotectic curve towards the Di–Ab or the Di–An eutectic?

(b)   Does non-equilibrium crystallization in the Di–Ab–An system result in liquids richer or poorer in CaO than those generated by equilibrium crystallization?

(c)   Look at the SiO_2 contents of diopside, albite and anorthite listed in Table 3. Is the composition of the liquid at P (Figure 25) richer or poorer in SiO_2 than that at the Di–Ab eutectic?

You should attempt SAQs 14–17 together before checking the answers.

SAQ 14 (*Objective 20*)   Table 6 presents the SiO_2 and Al_2O_3 contents of a suite of volcanic rocks collected from the Jebel al Abyad area in Arabia. Plot these data on a graph of Al_2O_3 against SiO_2 (Figure 37), join up the points by a smooth curve (as, for example, in Figures 34 and 35) and then answer questions (a), (b) and (c).

TABLE 6 SiO_2 and Al_2O_3 contents (in weight per cent) of selected volcanic rocks from Jebel al Abyad

Analysis no.	SiO_2	Al_2O_3
14	46.8	16.0
24	49.4	16.5
31	56.1	17.2
34	58.3	18.5
27	60.6	17.4
17	62.3	17.3
39	63.4	16.2
19	70.3	13.0
25	73.0	11.5

FIGURE 37   A graph of Al_2O_3 against SiO_2, for use with SAQ 14.

51
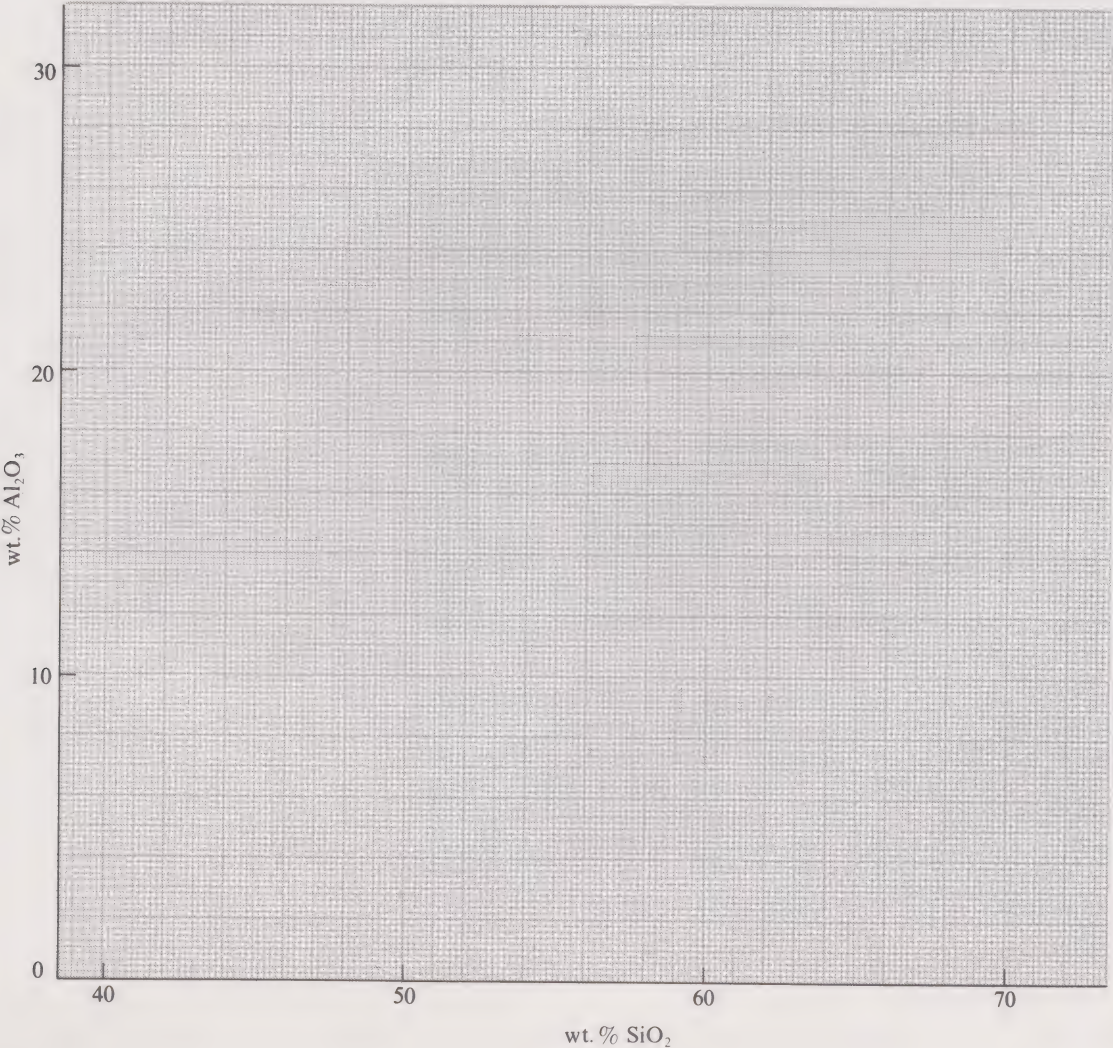
(a) Describe briefly the shape of the curve you have plotted on the graph of Al_2O_3 against SiO_2. Is it straight or kinked?

(b) In terms of fractional crystallization, what is the significance of a change in slope in the trend of the analytical data plotted on chemical variation diagrams such as Al_2O_3 against SiO_2?

(c) Assume that these rocks from Jebel al Abyad are related by fractional crystallization. Would you expect the Al_2O_3 and SiO_2 contents of the separated minerals (the extract) to be higher or lower than the liquids at (i) 47 per cent SiO_2 and (ii) 60 per cent SiO_2?

SAQ 15 (*Objectives 19 and 20*) Plot the SiO_2 and Al_2O_3 contents of the minerals in Table 7 on the same graph as the results from the Jebel al Abyad volcanic rocks.

Could the evolution of the liquid from 47 to 56 per cent SiO_2 be due to the crystallization and separation of any *one* of the minerals in Table 7 by itself?

SAQ 16 (*Objective 17*) The phenocrysts in the rocks suggest that olivine and plagioclase were the first two minerals to crystallize, and they are believed to have controlled the evolution of the liquid from 47 to 56 per cent SiO_2.

(a) What are the Al_2O_3 and SiO_2 contents of the mineral extract (plagioclase plus olivine) that could have controlled the evolution of the liquid from 47 to 56 per cent SiO_2? (*Hint* Refer back to Figures 31a and 32 if you are unsure of this.)

(b) What are the relative proportions (in per cent) of olivine and plagioclase in the mineral extract from SAQ 16(a)?

(c) How much crystallization (and separation) of the extract (olivine plus plagioclase) is needed to drive the composition of the liquid from 47 per cent to 56 per cent SiO_2?

SAQ 17 (*Objective 19*) In the volcanic rocks with more than 60 per cent SiO_2, Al_2O_3 starts to decrease as SiO_2 increases.

(a) How does this differ from the trend in the rocks with less than 58 per cent SiO_2?

(b) Can you suggest an explanation for this change in slope (or kink) in the trend of the analytical data at about 58 per cent SiO_2?

(c) Which mineral, or minerals, appear to influence most the evolution of the liquids from 60 to 73 per cent SiO_2?

6 Granites—from crust or mantle?

'Granite' is one of the major constituents of continental crust and how it forms is therefore central to our understanding of both the formation and the evolution of the continents. It was discussed briefly in Block 1, where it was emphasized that the term 'granite' is used variously by geologists. Granite in a strict sense is an intrusive rock consisting predominantly of quartz, alkali feldspar and plagioclase, with minor amounts of ferromagnesian minerals (typically biotite). Its chemistry is very *evolved* (these are all lower-temperature minerals), as it is rich in SiO_2 (greater than 70 per cent) and alkali elements, but low in iron, magnesium and calcium (see Block 1, Table 14, p. 68).

evolved rocks

Granite in a wider sense, by contrast, includes the whole family of quartz–feldspar-bearing intrusive rocks, which actually range in composition from granite (in the narrow sense) almost to *diorite*[A]. The majority are probably *granodiorites*[A] and diorites, and thus a reasonable estimate of the average composition of continental crust lies somewhere between these two—at about 60 per cent SiO_2 (see Block 2, Table 9 and associated discussion in Section 4.1). This is the composition of an average andesite and we can therefore consider similar techniques to those outlined earlier for the Dominica volcanic rocks.

Look back at Figure 34 (p. 46). Liquids of 60 per cent SiO_2 may be generated by 60–70 per cent fractional crystallization of a basaltic liquid—assuming for the sake of this discussion that the mineral assemblage that is removed has the same composition as the extract in ITQ 19 (Figure 66). Thus a piece of average continental crust could be formed by fractional crystallization of basaltic liquids derived originally by partial melting of upper mantle peridotite above subduction zones—that is, along destructive plate margins (Block 1, Figure 42) such as the Andean chain in South America. However, there are two noteworthy consequences of such a model:

TABLE 7 SiO_2 and Al_2O_3 contents (in weight per cent) of selected minerals from the Jebel al Abyad lavas

Mineral	SiO_2	Al_2O_3
Olivine	39.0	0
Plagioclase	50.0	31.8
Pyroxene	52.0	1.5
Alkali feldspar	63.5	20.6

1 The crystals that become separated from magmas during fractional crystallization presumably collect somewhere. If 70 per cent fractional crystallization takes place, then there should be about 2.3 km^3 of crystals for every cubic kilometre of andesite (or diorite–granodiorite) liquid (about 60 per cent SiO$_2$).

2 Basaltic liquid probably represents about a 20 per cent melt of peridotite: therefore for each cubic kilometre of andesite liquid there should also be about 13.3 km^3 of residual solid material left behind in the upper mantle.
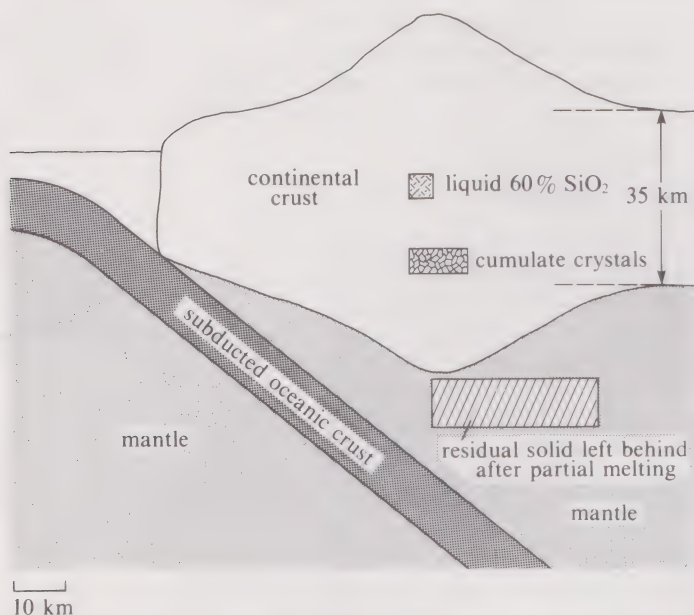

FIGURE 38   A schematic section through a continental destructive plate margin such as in the South American Andes. For discussion see text.

This model is illustrated in a schematic sketch section through a continental destructive plate margin (Figure 38). Continental crust is normally 30–35 km thick, but it may increase up to 70 km in areas of high mountains like the Andes and the Himalayas. In the latter, this unusual thickness is attributed to collision between two continents, while in the Andes it is thought to reflect the addition of new material (magma) to the crust above a subduction zone. In Figure 38 the size of the 'boxes' illustrates the relative quantities of andesite liquid, cumulate crystals and residual solid material left behind in the upper mantle—according to the model that we outlined above. Thus 333 km^3 of residual upper mantle material and 58 km^3 of crystals result from the generation of just 25 km^3 of intermediate liquid.

The significant point is that the residual solid material left in the upper mantle has had most of its low-temperature components removed by partial melting, that is, they went to make up the basaltic liquid. Thus the residual material consists predominantly of the higher-temperature minerals in the original peridotite and it follows that (a) it will only start to melt again at much higher temperatures, and (b) the chemistry of any liquid produced will be very different from that of common basalts—it will contain very much more olivine for example (see ITQs 1 and 3). In effect, therefore, suitable basaltic liquid from which to generate andesite or granite by fractional crystallization can only be produced *once* from any segment of upper-mantle peridotite.

Thus we must look again at the relative volumes of material shown in Figure 38. If just the uppermost 'bulge' of extra crust were of andesite composition (60 per cent SiO$_2$) and if it were derived by the model outlined here, then it would need *three times* more upper-mantle material than that depicted above the subduction zone in Figure 38.

Can you suggest how we might resolve this dilemma?

There are at present no certain answers, but some suggestions you might bear in mind include (a) a larger contribution of more SiO$_2$-rich (andesitic) material from the subducted oceanic crust; (b) convection in the upper mantle which would replenish those areas above the subduction zone with as yet 'unmelted' peridotite

(Figure 38); (c) perhaps, because it is so difficult to estimate the composition of the lower crust (as we discussed in Block 2), our estimate of the average composition of continental crust is wrong—perhaps it contains less than 60 per cent SiO_2.

A second problem is that the large volumes of crystals required by this model have simply not been found. In part, this may reflect the fact that it is often very difficult to recognize *cumulates* within coarse-grained intrusive rocks, but it also suggests that fractional crystallization may not play such an important role in the genesis of particularly the more SiO_2-rich granitic rocks. We must therefore consider other models for the generation of these rock types. Perhaps they can be derived by partial melting in the *crust*, as well as by fractional crystallization of magmas that were derived by partial melting in the mantle. To explore this possibility, we must return to the experimental laboratory and in particular look at the system quartz–albite–orthoclase.

6.1   The quartz–albite–orthoclase system

Since many granites in the strict sense contain over 75 per cent of quartz, albite and orthoclase, it is possible to make quite accurate comparisons between the compositions of liquids within the synthetic quartz–albite–orthoclase (Qz–Ab–Or) system and natural 'granites'. *Orthoclase* ($KAlSi_3O_8$) is a potassium or, more generally, an *alkali feldspar*[A]. Albite ($NaAlSi_3O_8$) we have already met in the diopside–plagioclase system (Figures 24 and 25), and it is interesting because it is in effect the cornerstone of the feldspar minerals (see Block 1, Section 3.3.4 and Figure 37). On one side, it exists in complete solid solution with anorthite in the plagioclase feldspars (Figures 16 and 19) and, on the other, it also undergoes *partial* solid solution with orthoclase under common geological conditions, these two together making up the alkali feldspars. Mixtures in the binary quartz–albite and quartz–orthoclase systems exhibit simple eutectic behaviour similar to that shown in Figure 12b, to An and Di (Figure 13), or to salt and water (Figure 15). The relationships between albite and orthoclase, however, are more complex. The system of these two feldspars shows both *partial solid solution* and a temperature *minimum*, the characteristics of which are explained more fully below.

orthoclase (potassium feldspar)

Figure 39 shows the alkali feldspar system under fixed pressure conditions. The general principles you have already studied also apply to the crystallization relationships between albite and orthoclase. Their system is like two separate plagioclase systems joined together at a common low temperature point. This point has a composition of about Or_{30} (70 per cent albite, 30 per cent orthoclase). Solid solution takes place on both sides of this minimum point (D in Figure 39) in just the same way as it does in the pure plagioclase system (Figure 16).
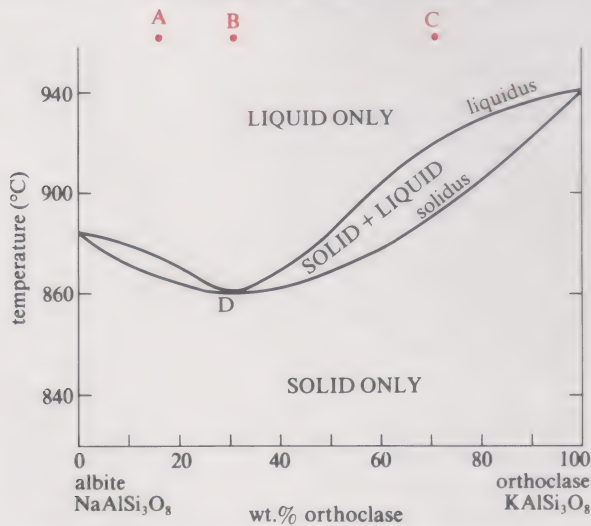
FIGURE 39   A binary system showing partial solid solution and a temperature minimum (D): the alkali feldspar system. For A, B and C, see ITQ 20.

Now find out whether you understand how to use such phase diagrams by answering ITQ 20.

> **ITQ 20**   (a)   What is the composition of the first crystals to form upon cooling melts of compositions A, B and C in Figure 39? Express your answer in per cent Or, for example 55 per cent Or, or Or_{55}.

(b)   Assuming that bulk equilibrium is maintained between the crystals and the liquid throughout crystallization, what is the composition of the last crystals to form just prior to complete solidification of samples A, B and C in Figure 39?

Contrast your answer to ITQ 20 (b) with what happens if fractional crystallization takes place in this system (Figure 39). As more and more crystals are removed, *all* liquids, *regardless of their starting composition,* move towards the minimum point D. This is arguably the most significant feature of the alkali feldspar system.

The minimum point D depicts the composition of the lowest temperature liquid which can exist in the Ab–Or system at this particular pressure. That is a feature it shares with a eutectic point in a binary eutectic system—but can you see what makes a temperature minimum *different* from a eutectic point?

How many minerals are in equilibrium with the liquid at the eutectic point in a binary eutectic system such as Di–An (Figure 13)?

The answer is two. The eutectic point is the only place in a binary eutectic system where *both* minerals (in that case, diopside and anorthite) can co-exist with the liquid. Compare that with the number of minerals in equilibrium with the liquid at the minimum point D in Figure 39.

What is the composition of the mineral(s) in equilibrium with the liquid at the minimum point D in Figure 39?

Crystals in equilibrium with a liquid plot on the solidus at the same temperature as that of the liquid. At the minimum point D in Figure 39, they therefore have the *same composition as the liquid.* Moreover, at equilibrium the crystals all have the same composition and thus, unlike the situation at the eutectic point, only *one* mineral can be in equilibrium with the liquid at a binary temperature minimum. All crystals at D have composition Or_{30}.

Another feature of the alkali feldspars with compositions near the middle of the Ab–Or range is that at temperatures below that of the minimum point (D in Figure 39) they begin to separate into discrete crystals rich in Or and Ab. This is due primarily to the disparity in ionic radius between K^+ (133 pm) and Na^+ (97 pm). They differ by about 35 per cent and thus contravene the general rule introduced in Block 1 (Section 3.2.2) that *one ion may replace another completely, to form a solid-solution series, if their size difference does not exceed 15 per cent of the radius of the smaller ion.* In the alkali feldspars, K^+ and Na^+ only manage to substitute for one another, and form a complete solid-solution series, at high temperatures. (See also Block 1, Figure 37.) A photograph of an intergrowth of discrete crystals which have separated out at temperatures below the solidus (Figure 39), is shown in Figure 40.
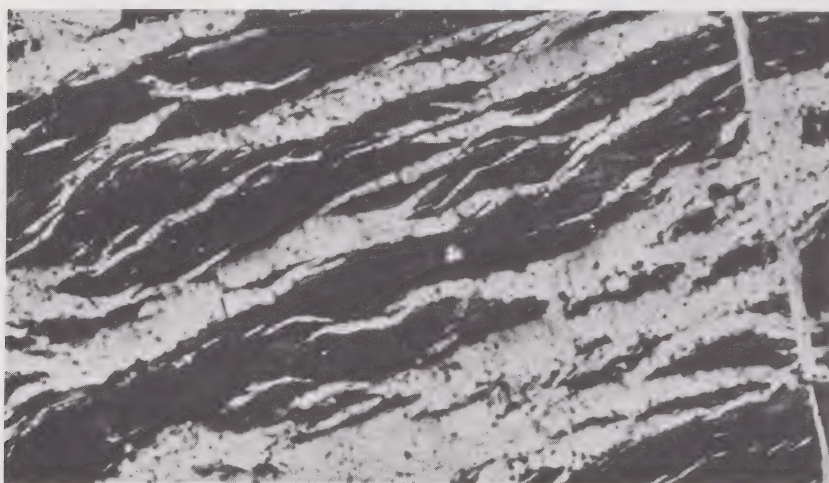

FIGURE 40   Photomicrograph of an alkali-feldspar intergrowth. Dark areas: albite; light areas: orthoclase. Each phase is homogeneous. (Magnification × 40.)

If we now put the three binary systems (quartz–albite, quartz–orthoclase and orthoclase–albite) together into a three-component Qz–Ab–Or system, the shape of the liquidus surface in a three-dimensional diagram of composition against

temperature looks like model 2 in your Home Experiment Kit (Figure 41). Figure 42 is the phase diagram, or temperature contour map of that system. It consists of two portions, the field in which quartz crystallizes first and the field in which the feldspars crystallize first, and its general form reflects that of its three simple binary systems.
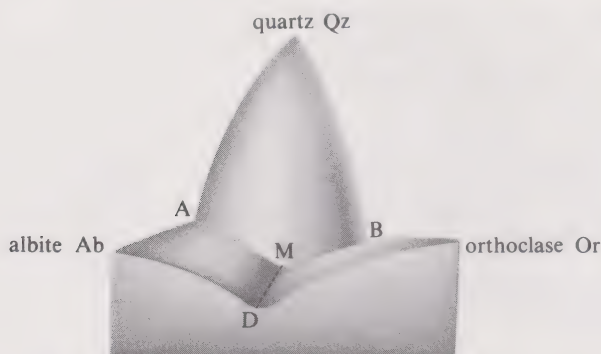

FIGURE 41   Block model showing the liquidus surface of the quartz–albite–orthoclase system (Home Experiment Kit model 2).
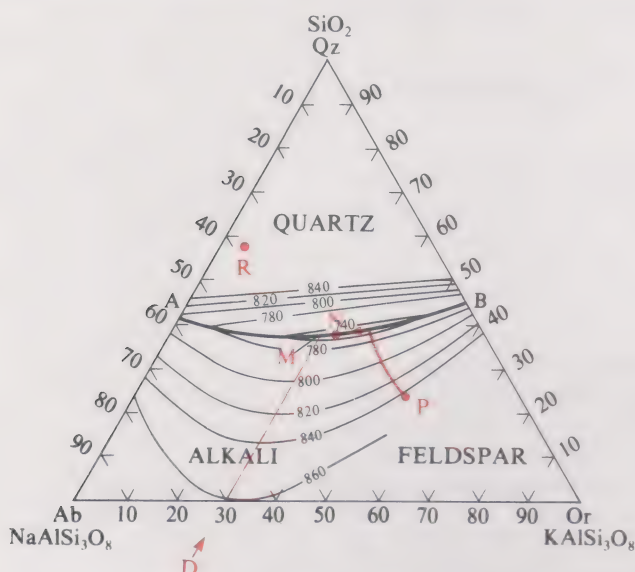

FIGURE 42   Diagram of the quartz–albite–orthoclase system at atmospheric pressure. For clarity, the contours for Qz- and Or-rich compositions have been omitted. (For explanation of the letters, see text.)

Thus quartz–albite and quartz–orthoclase have *eutectic points* at A and B respectively; in three dimensions these are joined by a cotectic curve AMB (Figures 41 and 42). This curve has the same characteristics as the cotectic curve we discussed in the Di–Ab–An system (Figure 25), but it is unusual in that it slopes 'downhill' *towards M* from *both* the eutectic points A and B; M is the lowest point on the curve AMB.

> Look at model 2 from the side of the albite–orthoclase system (Figure 41). Can you suggest why the cotectic curve AMB has its 'basin-like' form and does not, for example, just slope 'downhill' continuously from A to B?

The answer lies in the form of the liquidus curve in the binary feldspar system albite–orthoclase—the cotectic curve AMB reflects (although at a lower temperature) the form of the liquidus curve (Ab–D–Or) in Figure 39. The dashed line DM marks the composition and the temperature of the minimum point (for example, D in Figure 39) for compositions that have more and more quartz (that are nearer the quartz apex).

In summary, the system Qz–Ab–Or is dominated by the quartz and alkali feldspar stability fields. They, in turn, are separated by a cotectic curve (AMB) running between the quartz–albite (A) and the quartz–orthoclase (B) eutectics. This cotectic curve lies in a slightly unusual *thermal 'valley'* in that one side (the quartz-rich side) is very much steeper than the other and that the valley floor runs 'uphill' in both

thermal valley

directions from M, towards both A and B. In reality, the valley is a 'basin' in that the liquidus surface slopes downhill (down-temperature) from all compositions to a single point M. This is commonly called the *granite minimum*, and its composition is nearly equivalent to that of many naturally occurring granites. You will see in a moment why this should be so.

granite minimum

Let us now consider the crystallization path of a particular melt P (Figure 42) in the Qz–Ab–Or system. Since no new principles are involved, it is presented in a series of questions and answers and we suggest that you should make a serious attempt to answer the questions on your own before seeking help from the answers.

> What is the temperature at which the first crystalline phase starts to separate from a melt of composition P?

840–845 °C.

> What is the first crystalline phase to separate upon cooling a melt of composition P?

P plots in the alkali feldspar field (Figure 42), thus the first crystals are of alkali feldspar.

> Will that first alkali feldspar contain more or less orthoclase than the liquid from which it crystallized?

More. Qualitatively this can be seen by comparing the liquidus and solidus curves for orthoclase-rich compositions in Figure 39. Remember, however, that Figure 39 is for the pure Ab–Or system and it is not directly applicable to compositions that contain a third component—in this case quartz (see Figure 24 and the discussion of the Di–Ab–An system).

> As the temperature falls, how will the composition of the melt change?

The melt (or liquid) is experiencing two effects:
(i) The feldspar that is crystallizing is richer in orthoclase than the liquid, and thus the latter must be getting richer in albite.
(ii) Because feldspar is crystallizing, the melt must be also getting richer in quartz. The net result is that the melt moves along a curved path towards the cotectic curve AMB.

> What happens when the melt reaches the cotectic curve?

Quartz will start to crystallize, and, with continued crystallization of feldspar and quartz, the melt composition will move along the cotectic towards the minimum M.

> Assuming that complete equilibrium is maintained between the crystals and the liquid, what is happening to the feldspar composition in the meantime?

It is changing by reaction with the melt, and its composition becomes richer in albite as the melt moves *towards* the minimum M. In principle, this is the same as equilibrium crystallization in the binary Ab–Or system (Figure 39). However, the temperature of the minimum in that system (D) is higher than that in the ternary Qz–Ab–Or system (point M in Figures 41 and 42).

> As the temperature falls and the liquid moves along the cotectic curve, what will be the composition of the last crystals to form before solidification is complete?

The last crystals to form will be quartz and alkali feldspar, which has the same composition as the feldspar in the original liquid (about Or_{70}). (Again this assumes that crystallization took place under equilibrium conditions.) The liquid in equilibrium with these last crystals lies on the cotectic curve AMB at about point N (Figure 42).

> In the absence of fractional crystallization, what will be the bulk composition of the final product?

It will have the same overall composition as the melt we started with, P.

But supposing there had been fractional crystallization, that is, removal of earlier formed crystals during cooling to prevent their continued reaction with the melt. What would then be the composition of the final liquid?

Fractional crystallization drives all liquids towards the composition of the granite minimum M—which would therefore be the composition of the final liquid.

ITQ 21 Trace for yourself the crystallization path of a liquid of composition R (Figure 42), both (a) under equilibrium, and (b) under non-equilibrium conditions.

You will, we hope, now appreciate that phase relations in the synthetic granite system suggest that, under conditions of fractional crystallization, liquid containing quartz and alkali feldspar will always finish crystallizing in a rather restricted area of the system near the granite minimum. If naturally occurring granites originated by fractional crystallization, as suggested earlier, their compositions should lie near to that of the granite minimum. To assess this hypothesis, the composition of a large number of analysed granitic rocks have been recalculated into quartz, albite and orthoclase molecules and plotted on the phase diagram. The results are shown in Figure 43. There is a striking concentration of points within a small area close to the granite minimum (Figure 42), which suggests that these granites *could* have originated by processes of fractional crystallization of silicate liquids. However, there is another process which could also explain why many granites lie so close to this minimum.
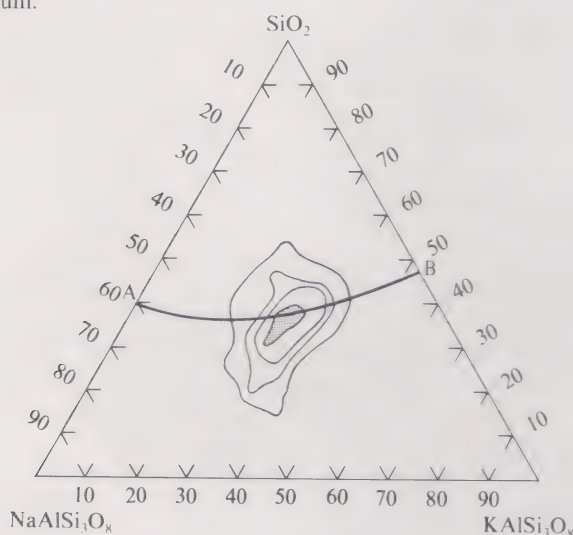

FIGURE 43   Compositions of over 500 analysed granitic rocks recalculated as molecules of quartz, albite and orthoclase. The results have been contoured on the basis of frequency and 90 per cent of the analyses fall in the shaded area in the centre. The curve AB is the cotectic curve for the Qz–Ab–Or system at pressure of 2 kbar.

Can you recall what this might be?

It is the process of *partial* melting, which corresponds in a *general* way (there are detailed differences) to the reverse of fractional crystallization. That is to say, as a solid is heated the *first* part to melt is the lowest-temperature melting fraction, which is the *last* part to solidify in the reverse process of fractional crystallization. In the case of granites we may be more specific: fractional crystallization of *any* mixture of alkali feldspars and quartz leads to the production of a final crystalline end-product with a composition close to the granite minimum. Conversely, if *any* mixture of alkali feldspars and quartz is heated until it begins to melt, the composition of the first formed melt will lie on the cotectic curve fairly close to the granite minimum. *Thus both partial melting and fractional crystallization processes may account for the abundance of naturally occurring rocks with compositions around the granite minimum.*

Many rocks of intermediate composition (andesites and diorites) contain significant amounts of quartz, alkali feldspars and plagioclase (see Block 1, Figure 41). Thus, from our discussions of the phase relations in the synthetic Qz–Ab–Or system, we would predict that partial melting of rocks with intermediate SiO_2 contents should

produce liquids with compositions of 'granite'. Experimental work on natural rocks has confirmed that prediction and thus most geologists now accept that granitic rocks are generated by different processes under different circumstances. Some reflect fractional crystallization of basic 'primary' magmas derived by partial melting within the upper mantle, others are partial melts of pre-existing continental rocks. There is also a third possibility which is at present receiving a lot of attention, namely that mantle-derived magmas may be 'contaminated' with continental material as they pass through the crust. All three processes result in rocks with very similar major-element compositions (that is, at or near the granite minimum) and thus it is almost impossible to distinguish the relative roles of each process solely on the basis of major-element analyses. Instead, as we shall see in Section 8, it becomes necessary to evaluate the variations in trace elements and in isotope ratios in such rocks.

6.2 Summary of Section 6

The ternary system Qz–Ab–Or is unusual in that the liquidus surface everywhere slopes down towards an approximately central minimum point (M), generally referred to as the *granite minimum*. Consequently:

(a) Fractional crystallization of all samples in this system drives the composition of the residual liquid towards that of the granite minimum—irrespective of their initial composition.

(b) Conversely, on heating a rock consisting largely of quartz and alkali feldspar, the first liquid to form is also similar in composition to the granite minimum.

In practice, it is now generally agreed that granitic rocks are formed by different processes under different circumstances. They can reflect fractional crystallization of basaltic magmas and/or partial melting of more SiO_2-rich material already present in the crust. Significantly the latter simply represents *remelting* or '*reworking*' of pre-existing continental crust, and it contrasts with the fractional crystallization of basaltic (and hence mantle-derived) magmas which offers a mechanism by which *new material is added to the crust.*

6.3 Objectives for Section 6

Now that you have completed Section 6, you should be able to:

1 Define in your own words, or recognize valid definitions of, the terms flagged in the margins of this Section.

21 Describe equilibrium and non-equilibrium crystallization and melting in the binary system Or–Ab.

22 Discuss partial melting and crystallization in the synthetic granite system Qz–Ab–Or.

23 Outline briefly two ways in which intermediate and acid (granitic) magmas may be formed.

Apart from Objective 1, to which they both relate, the two ITQs in this Section test these Objectives as follows: ITQ 20: Objective 21; ITQ 21: Objective 22.

You should now do the following SAQs, which test other aspects of these Objectives:

SAQ 18 (*Objective 21*) Consider a solid sample of Or_{20} (20 per cent orthoclase, 80 per cent albite) in the simple binary system Or–Ab. Assuming that melting takes place under equilibrium conditions, use Figure 39 to estimate:

(a) The temperature and the composition of the *first* liquid to form as the temperature is raised.

(b) The temperature and the composition of the *last* crystals before the sample becomes completely liquid.

SAQ 19 (*Objective 22*) A sample consists of 20 per cent quartz, 70 per cent albite and 10 per cent orthoclase. Plot this on the triangular diagram SiO_2–$NaAlSi_3O_8$–$KAlSi_3O_8$ (Figure 42) and answer the following questions:

(a) On cooling, which mineral crystallizes first?

(b) Do those first crystals contain more or less orthoclase than the co-existing liquid?

(c) At what temperature do the first crystals appear?

(d) Assuming that complete equilibrium is maintained throughout crystallization, does the feldspar become richer in albite or orthoclase as the temperature falls?

(e) If cooling takes place quickly so that zoned feldspar crystals are formed, are the centres of these crystals likely to be richer in albite or orthoclase than the edges?

(f) At approximately what temperature will the first crystals of quartz appear?

(g) If crystallization takes place under equilibrium conditions, will the last drop of liquid have the same composition as the granite minimum (M)?

SAQ 20 (*Objective 23*) Give two objections to the suggestion that most high-SiO_2 igneous rocks generated along a destructive plate margin such as the Andes were produced by fractional crystallization of basaltic liquids alone. Give your reasons in a couple of sentences.

7 Trace elements in igneous processes

Study comment The previous Sections have illustrated how major- and minor-element analyses of rocks and minerals may be combined with experimentally determined phase relations to interpret suites of igneous rocks. However, ambiguities remain and much more may be learnt about igneous processes by also considering the distribution of *trace elements* and *radiogenic isotopes*. As we shall see now these are handled using different techniques—moreover, since the commonly used radiogenic isotopes occur in trace elements, the two are discussed in Sections 7 and 8, which are closely linked.

Over eighty naturally occurring elements make up less than one per cent of the Earth by weight. Yet many of these so-called *trace elements*[A] have an importance that far outweighs their abundance. Their very scarcity gives them value, be it traditional (gold and silver) or industrial (platinum or rhenium), and considerable time and money have been invested in studying the natural processes by which such elements become concentrated into ore bodies. A few emit radiation; they are thus radioactive and therefore play vital roles in generating the heat within the Earth (this will be discussed in Block 4) and in fulfilling our own immense energy requirements. Some of these are now used as radiometric 'clocks', thus enabling us to date geological events throughout Earth history. Finally, and perhaps most significantly, geologists have learnt much from the study of trace elements because they are so sensitive to their physical and chemical environment. *Major elements*[A] form minerals and their distribution influences which particular minerals are present. Trace elements, by contrast, rarely form minerals of their own, and they are therefore forced to seek 'sites' in what are inevitably slightly alien crystal structures (Block 1, Section 3.2.2). However, it is precisely this need for compromise between the nature of the trace element and the proffered sites in the available minerals that makes the study of trace elements so invaluable. Their distribution between minerals and a fluid, be it magma or water, is extremely sensitive to parameters such as the composition of the fluid, oxidation state, temperature and, to a lesser extent, pressure—in addition to the major-element compositions of the minerals.

In Section 5, we considered how major-element geochemistry might be combined with experimentally determined phase relations to provide information on the evolution and ultimate origins of igneous rocks. Apart from a brief introduction in Block 1, Appendix 1, trace elements have been largely ignored until now because, as we shall see, they are best handled using different techniques. Many such elements have been used to understand a variety of geological problems, but in this Section we shall restrict ourselves to half a dozen which are used widely in the study of igneous processes: rubidium (Rb), strontium (Sr), barium (Ba), zirconium (Zr), yttrium (Y) and nickel (Ni). *Minor elements*[A] such as potassium (K), phosphorus (P) and titanium (Ti) may also be profitably considered along with the trace elements.

7.1 Mineral analyses, partition coefficients, and fractional crystallization

The trace-element contents of minerals in igneous rocks have traditionally been determined on separated minerals. The rock is crushed to a coarse powder and samples of each mineral are isolated either on the basis of differing density or magnetic properties. If extremely pure samples are required, the mineral grains may be picked out by hand, using a powerful binocular microscope, and then washed in dilute acids. The trace-element concentrations are usually determined by *neutron activation analysis*[A] or *mass spectrometry*[A] (Block 1, Appendix 1).

In general, we want to analyse minerals that are in equilibrium with each other and with the liquid from which they crystallized. Hence it is desirable to obtain samples of both minerals and liquid from the same rock—the composition of the liquid being given by the bulk analysis of *all* the minerals making up the fine-grained *groundmass* (see Figures 36 and 14). Sometimes it is difficult to obtain suitable samples of the groundmass material, and, if so, it may be necessary to analyse the bulk sample instead—providing that on chemical and textural grounds (see Figure 36 and ITQ 17) it too is believed to represent a liquid.

> Will the composition of the liquid obtained by analysing the bulk sample be more or less evolved than that obtained from the groundmass?

The bulk sample effectively represents the composition of the liquid *before* the phenocrysts formed and thus it will be less *evolved* (or more *primitive*) in composition than the groundmass which represents the liquid *after* the phenocrysts formed. Hence, to suggest that a phenocryst mineral was in equilibrium with a liquid with the same composition as its *bulk rock* (that is, phenocrysts plus groundmass), is to introduce an approximation which sometimes we have little choice but to accept.

primitive rocks

Figure 44 is a chemical variation diagram on which are plotted the Sr (in parts per million, p.p.m.) and SiO_2 (in weight per cent) contents of three igneous minerals (olivine, plagioclase feldspar and a pyroxene), a basalt B, and an andesite A. Using the mixing calculation introduced in Section 5.2, we may estimate how much fractional crystallization of the different minerals is required to change the composition of the liquid from that of basalt B to that of andesite A. Make sure that you can do ITQ 22.

> **ITQ 22** Use the mixing calculation to determine how much fractional crystallization of olivine is required to change the composition of the liquid from B to A in Figure 44.
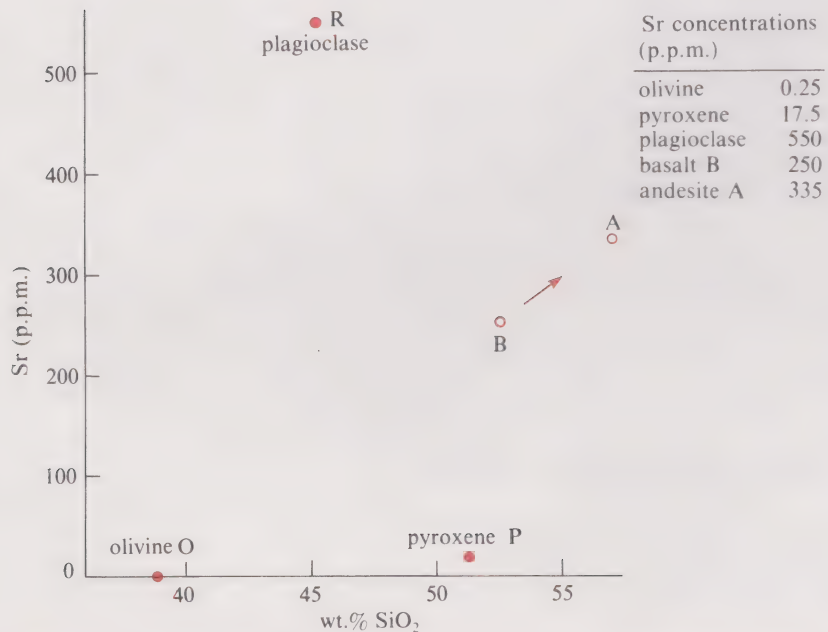
FIGURE 44   Chemical variation diagram of Sr against SiO_2 for three minerals (olivine O, plagioclase R, and pyroxene P), a basalt B, and an andesite A.

Sr concentrations (p.p.m.)	
olivine	0.25
pyroxene	17.5
plagioclase	550
basalt B	250
andesite A	335

However, it is also possible to calculate how much fractional crystallization of olivine is required using either the Sr or SiO_2 contents of olivine, basalt B and andesite A.

In the mixing calculation we measured off distances on Figure 44. Hence

$$\text{percentage of olivine fractionation} = \frac{100\,(BA)}{OA}$$

If, for example, we consider only the Sr contents, we may also write

$$\text{percentage of olivine fractionation} = \frac{100(C_B - C_A)}{C_O - C_A}$$

where C is the concentration of Sr in the different phases—olivine (O), basalt (B) and andesite (A). Thus, using the Sr contents from Figure 44,

$$\text{percentage of olivine fractionation} = \frac{100\,(250 - 335)}{0.25 - 335}$$

$$= \frac{-8\,500}{-334.75}$$

$$= 25$$

that is, the same answer as you obtained using the graphical method in ITQ 22. Moreover, we have arrived at an extremely simple technique with which to calculate the effects of fractional crystallization, using merely the concentrations of a trace element in the liquid and the crystallizing minerals.

As indicated in the introduction to this Section and in Block 1, Appendix 1, trace elements are usually present in such small amounts that they rarely, if ever, form minerals of their own. Thus, in contrast to major elements, their concentration in the liquid is not going to *influence* which minerals will crystallize and what their compositions may be. Rather the behaviour of a trace element merely *reflects* which mineral(s) crystallize and the conditions under which crystallization takes place. If a particular mineral is in equilibrium with a melt of 25 p.p.m. Sr or 250 p.p.m. Sr, the *relative* effect on the Sr content of the melt should be the same. In each case, a particular mineral will take up the same percentage of the Sr present in the melt, that is, if it is going to accommodate 10 per cent of the Sr in its structure, it will contain 2.5 or 25 p.p.m. respectively, depending on which melt it was in equilibrium with.

This essentially passive role played out by trace elements in most igneous processes allows us to describe their distribution between two phases (e.g. two minerals, or a mineral and a liquid) in terms of a *partition coefficient* (K_D),

partition coefficient, K_D

$$K_D = \frac{\text{concentration of trace element in phase 1}}{\text{concentration of trace element in phase 2}}$$

K_D is constant for any particular equilibrium. For a mineral in equilibrium with a liquid, partition coefficients are conventionally written so that the concentration of the trace element in the mineral is divided by that in the liquid. Clearly, in practice we analyse igneous rocks, which were once liquids, rather than the liquids themselves. Thus, for plagioclase in equilibrium with basalt B in Figure 44, the partition coefficient for Sr is given as

$$K_D = \frac{\text{concentration of Sr in plagioclase}}{\text{concentration of Sr in basalt B}}$$

$$= \frac{550}{250}$$

$$= 2.2$$

Similarly, the partition coefficient for Sr distributed between olivine and basalt B (Figure 44) is given by

$$K_D = \frac{\text{concentration of Sr in olivine}}{\text{concentration of Sr in basalt B}}$$

$$= \frac{0.25}{250}$$

$$= 0.001$$

ITQ 23 (a) Calculate the partition coefficient (K_D) for Sr distributed between pyroxene and basalt B in Figure 44.

(b) For Sr, the K_D for plagioclase is much higher than those for both olivine and pyroxene (see above and part (a) of this ITQ). Using Figure 44, can you deduce what relationship exists between the size of the individual partition coefficient (K_D) and whether the Sr content of the liquid will increase or decrease during crystallization of the particular mineral in question?

From the answer to ITQ 23 (b) three general points should be noted about the relationship between the size of the partition coefficient K_D and the change in the concentration of the trace element in the liquid during crystallization.

---

1 If K_D is less than 1, as is the case for Sr in olivine ($K_D = 0.001$) and pyroxene ($K_D = 0.07$), then crystallization of these minerals *increases* the concentration of the trace element in the liquid. Trace elements with small partition coefficients tend to stay in the liquid and thus, as crystallization proceeds, their concentrations will increase simply because the amount of liquid is being reduced.

2 If K_D is equal to 1, the concentration of the trace element in the mineral is the same as that in the liquid and clearly the latter does *not* change during crystallization.

3 When K_D is greater than 1 (for example, Sr in plagioclase, $K_D = 2.2$) the concentration of the trace element in the liquid is *reduced* by crystallization.

These points are further illustrated in Figure 45, which shows how changes in the concentration of a trace element in the liquid vary with the amount of crystallization and the size of the partition coefficients.
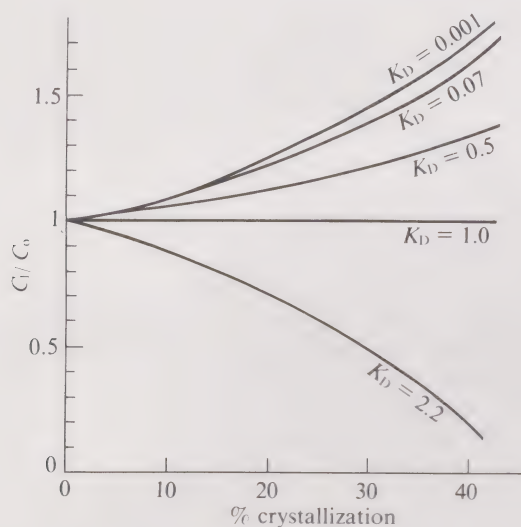
FIGURE 45 Graphs of C_l/C_o (the concentration of a trace element in the residual liquid C_l, divided by that in the original liquid C_o) against per cent crystallization for minerals with different partition coefficients (K_D). The curves are based on results from mixing calculations (see text).

We may conclude that in all but the special case of $K_D = 1$, crystallization affects the concentration of an element in the liquid. Fractional crystallization should therefore result in significant variations in the trace-element contents of a suite of related rocks.

Notice also that elements which have K_D greater than 1 are often described as '*compatible*', while those with K_D less than 1 are called '*incompatible*'; that is, they find it difficult to substitute into the particular crystal structure of the mineral which is crystallizing (as we shall discuss in Section 7.2). Thus, for example, Sr is compatible in plagioclase but incompatible with respect to olivine and pyroxene crystallization (Figure 44).

compatible elements
incompatible elements

Table 8 summarizes partition coefficients for a few selected trace elements distributed between basaltic magmas and minerals that are commonly in equilibrium with them—either in peridotite from which such magmas are derived, or within the basalts during crystallization.

TABLE 8   Selected trace-element partition coefficients. K_D = concentration in mineral/concentration in liquid.

	K	Rb	Sr	Ba	Zr	Y
olivine	0.001	0.001	0.001	0.001	0.01	0.01
orthopyroxene	0.001	0.001	0.01	0.001	0.03	0.2
clinopyroxene	0.002	0.001	0.07	0.001	0.1	0.5
garnet	0.001	0.001	0.001	0.002	0.3	2.0
plagioclase	0.2	0.07	2.2	0.2	0.01	0.03

With just two exceptions, Sr in plagioclase and Y in garnet, all the partition coefficients in Table 8 are less than 1, and many of them are very small indeed. Thus for *basaltic* magmas in equilibrium with most common minerals the overwhelming majority of trace elements are incompatible. Another exception, not given in Table 8, is nickel (Ni) which is compatible in olivine: its partition coefficient is very sensitive to the composition of the magma and varies from 3 to 10 for olivines in equilibrium with basaltic magmas.

If we now compare the data in Table 8 with the curves in Figure 45 we may derive two extremely important general statements:

1   *Because high partition coefficients* $(K_D > 1)$ *are rare, when they do occur they are characteristic of the particular mineral.* Only if K_D is greater than one will the concentration of a trace element in the liquid *decrease* with *increasing* fractionation (Figure 45). Thus, if Sr, for example, decreases in a suite of rocks which on the basis of their major-element compositions (as in Figures 34 and 35, for example) are thought to be related by increasing fractional crystallization in a subsurface magma chamber, then we could confidently conclude that plagioclase was one of the fractionating minerals. Similarly, decreasing Y and Ni concentrations are the telltale signs that garnet and olivine respectively had been crystallizing.

In Block 2 (Section 4.2.2) it was pointed out that the aluminium in undepleted peridotite is situated in plagioclase feldspar, *spinel*[A], or garnet depending on the pressure (Block 2, Figure 90). Similarly, for magmas crystallizing at different depths, the alumina-rich mineral will be plagioclase at low pressures, spinel at intermediate pressures, and garnet at high pressures. For brevity, only plagioclase and garnet are included in Table 8.

2   *The ratio of the concentrations of two incompatible trace elements* $(K_D < 1)$ *in a liquid will not be changed significantly by processes of fractional crystallization.* Compare the curves for $K_D = 0.001$ and $K_D = 0.07$ in Figure 45. Even though these partition coefficients differ by a factor of 70, the curves are remarkably similar; that is, the concentration in the liquid of trace elements with these and similar partition coefficients increases at similar rates as crystallization proceeds.

This point is illustrated by ITQ 24.

> **ITQ 24**   A basaltic magma contains 1 p.p.m. Rb and 10 p.p.m. Sr. Using the curves in Figure 45, estimate the Rb and Sr contents and thus the Rb/Sr ratio of the magma after 40 per cent fractional crystallization of clinopyroxene (K_D for Rb = 0.001, K_D for Sr = 0.07, Table 8). What is the percentage change in the Rb/Sr ratio of the magma during fractional crystallization?

Changes in the Rb/Sr ratio of the liquid with increasing clinopyroxene crystallization are illustrated in Figure 46. Even after 50 per cent crystallization, the Rb/Sr ratio has changed by less than 4 per cent, and to achieve a 10 per cent variation in Rb/Sr it is necessary to postulate more than 90 per cent crystallization. When you remember that after 50 per cent crystallization both elements have roughly *doubled* their concentrations in the liquid, and that the errors in many trace-element analyses are 1–10 per cent (depending on the technique and the element being analysed—Block 1, Appendix 1), you can see that a 4 per cent change in Rb/Sr is not very significant.
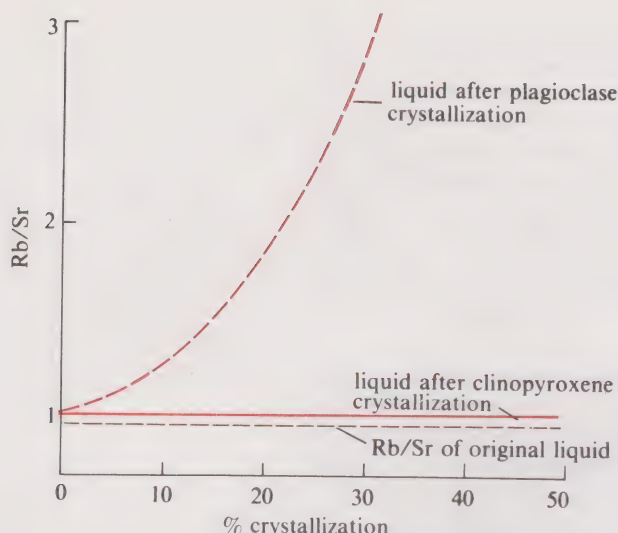
FIGURE 46   Rb/Sr against per cent crystallization illustrating how the Rb/Sr ratio in a liquid (magma) changes during progressive crystallization of pyroxene and plagioclase.

In summary, we have reached two important conclusions: first, variations in the *concentrations* of trace elements in a suite of igneous rocks reflect *how much* fractional crystallization (and, as we shall see later, partial melting) has occurred. Second, even where fractional crystallization has taken place, the *ratios* of incompatible element concentrations should be similar to those in the *original* (*primary*) *magma*.

It follows that: (a) we can use the ratios of incompatible trace elements in rocks produced by fractional crystallization to estimate those ratios in the original magma; and (b) we can assess whether two igneous rocks could have been derived by fractional crystallization from *similar* original magmas, depending on whether or not the two rocks have similar incompatible trace-element ratios; that is, if such ratios are very different, the rocks are unlikely to have been derived from similar original magmas.

Finally, would you expect the ratio of a compatible and an incompatible trace element to change significantly during fractional crystallization?

By definition, a compatible element ($K_D > 1$) is concentrated in the crystallizing mineral while the incompatible element ($K_D < 1$) is concentrated in the liquid. Consequently, the ratio of two such elements (in the magma) will change rapidly during fractional crystallization. This is illustrated in Figure 46, when plagioclase is crystallizing. Rb is incompatible and Sr is compatible—the Rb/Sr ratio in the magma thus changes by a factor of three after only 30 per cent crystallization of plagioclase. This contrasts with the very small change in Rb/Sr in the liquid which occurs after even 50 per cent crystallization of clinopyroxene (Figure 46). Remember also that only *two* of the partition coefficients listed in Table 8 are greater than one. Trace-element ratios do not therefore change very often during fractional crystallization, and, when they do (as in the case of Rb/Sr), then it is usually diagnostic of the mineral concerned (in that case plagioclase).

Similarly, trace-element ratios that include Y or Ni will change if garnet or olivine is crystallizing.

7.2   Factors that influence trace-element partitioning

We have seen that partition coefficients can vary by several orders of magnitude (Table 8). What do these variations reflect? Why is it for example that Sr substitutes readily into plagioclase feldspar and yet Rb does not?

Much of what we understand of these problems stems from the pioneering work of a scientist who is often regarded as the father of geochemistry—V. M. Goldschmidt.

Between 1922 and 1926 he and his associates at the University of Oslo worked out the structures of many compounds, thus establishing a basis on which to found general laws governing the distribution of elements in crystalline materials. In 1929, Goldschmidt moved to Göttingen, where he was to stay for six years working on the geochemistry of individual elements. He demonstrated that the two most influential factors governing whether an element could substitute into a particular crystal structure were the *ionic radius*[A] and the *ionic charge*[A]. The trace elements that find it easiest to obtain sites in a crystallizing mineral are those that have ions of similar size and charge to one of the major elements in the crystal structure. Thus Rb^+ (147 pm) commonly substitutes for K^+ (133 pm), and Sr^{2+} (112 pm) substitutes for Ca^{2+} (99 pm) in a wide range of silicate minerals.

We may now look in a little more detail at this relationship between the ionic size and charge of a trace element and those of the major elements it might replace in a particular mineral structure. We have chosen clinopyroxene as our example and Figure 47 illustrates how the size of the partition coefficients (K_D) varies with ionic
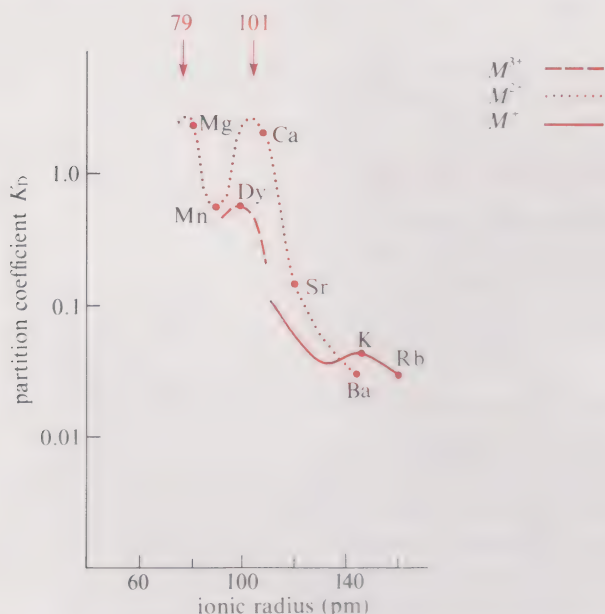

FIGURE 47 Variation of partition coefficients with ionic radius for M^+, M^{2+} and M^{3+} ions, distributed between pyroxene and groundmass crystals in a basalt from Tahiti.

radii for a number of different elements distributed between the pyroxene crystals and a fine-grained groundmass (which was the liquid) in a basalt from Tahiti. Since ions of different *charge* have been plotted, such a diagram enables us to assess the relationship between the *charge* and *size* of an ion and the *ease with which it can substitute into a particular mineral*—as expressed in the size of the partition coefficient. (Remember that if $K_D > 1$ the element goes preferentially into the crystals, while if $K_D < 1$ the element tends to remain in the liquid.)

What can you remember about the crystal structure of the *pyroxene*[A] mineral group?

Their basic skeleton is one of a *chain* of silicate tetrahedra, hence the name *chain silicates*[A] (Block 1, Section 3.3.2). Each silicate tetrahedron is joined to two others and alternate tetrahedra point outwards from the chain in opposite directions. These chains are then joined together by cations (Block 1, Figure 30), which in practice are the major zones of weakness in the pyroxene structure. Those zones result in very fine cracks, or *cleavage traces* (*CB*, Plate 15), and it is the ions in those zones that are most easily replaced by trace elements.

In the basic pyroxene structure, the common cations are Mg^{2+} and Fe^{2+} and a *solid-solution series* exists between $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$. These are the *orthopyroxenes*. However, most pyroxenes also contain a small amount of Ca^{2+}, and since Ca^{2+} ions are 20 per cent larger than Mg^{2+} or Fe^{2+}, they inevitably distort the pyroxene structure. Calcium-rich pyroxenes are called *clinopyroxenes* and the major cations in our example in Figure 47 are Mg^{2+} and Ca^{2+}. (See also Section 5.4.)

In Figure 47 there are three different curves linking ions of the same *valency*[A] (M^+, M^{2+} and M^{3+}). Which curve plots above the other two, at least over most of the diagram? What does that tell you about the relative ease with which M^+, M^{2+} and M^{3+} ions can substitute into the structure of this pyroxene mineral structure?

The curve for divalent ions (M^{2+}) plots above the other two for ions with ionic radii less than 140 pm. Thus, if ions of similar *size* but different *charge* are competing for a place in the pyroxene lattice, the results in Figure 47 indicate that divalent ions will be most readily accepted, that is, at a particular ionic radius they have the higher partition coefficients.

The second, and arguably the most striking feature about the curves on Figure 47, is the two maxima that occur at about 79 pm and 101 pm. These represent the optimum ionic sizes for substitution in this pyroxene structure. We may conclude that a trace element that is stable as a divalent ion (M^{2+}) and has an ionic radius of 79 pm or 101 pm has the best chance of being incorporated into the crystallizing pyroxene.

Why should that be so?

Precisely because those radii are slightly smaller than and the charge is the same as those of the ions that are most readily replaced in the pyroxene structure—in our example, Mg^{2+} and Ca^{2+}.

What then can we say about the *relative* roles of ionic size and charge in influencing whether a particular trace element may be incorporated into these pyroxene crystals?

Look particularly at the partition coefficients for dysprosium (Dy^{3+}), manganese (Mn^{2+}) and strontium (Sr^{2+}) in Figure 47: despite the general tendency for divalent ions to have the higher partition coefficients, out of these three it is the trivalent ion (Dy^{3+}) that is accepted most readily into the pyroxene structure. Thus, if ions of the *same size* but *different charge* are available then the divalent ions are accepted in preference to others. However, if the *sizes* of the ions also vary, then size can become more important than charge. Ions closest in size to the optimum values for pyroxene may be preferred—even when they are not of the desired M^{2+} valence state.

In summary:

(i)   High partition coefficients characterize ions of trace elements that are similar in size and charge to those of the major-element cations in the particular crystal structure.

(ii)   Most trace elements are not readily accepted into mineral structures. For ions of *different sizes* but the *same charge*, those closest in size to that of the available sites in the crystallizing minerals will have the higher partition coefficients. Conversely, if two ions have the *same size* but *different charges*, the one whose charge is closer to that of the available site will be preferred. When ions of *different sizes* and *different charge* are competing for the same site, the relationship can be very complex: and, as we saw in the case of Dy^{3+} and Sr^{2+}, the *size* of an ion may be more critical than its *charge* in determining the magnitude of its partition coefficient.

What happens if, because of its size, an M^{3+} ion substitutes in a site which, on the basis of charge only, would prefer an M^{2+} ion? How can the total charge be balanced?

Often by *coupled substitution*[A]: an M^{3+} ion might combine with an M^+ ion to replace two M^{2+} ions. The example discussed in Block 1, Section 3.2.2, was for major elements: Ca^{2+} and Al^{3+} substituting for Na^+ and Si^{4+} in the plagioclase feldspars.

7.3   Partial melting—a model for trace-element variations

Melting is, at least in the thermal sense, the reverse of crystallization. Rocks melt over a range of temperature throughout which the minerals present in the rocks may interact with the liquid being formed. These interactions and thus the evolution of the liquid can be described in terms of the distribution of trace elements between the minerals and the melt.

There are several general points to remember when discussing partial melting processes:

1 The characteristics of the minerals have not changed; they are the same as they were in the previous Section (see Table 8). Thus, residual garnet in the zone of melting will *preferentially retain* Y, for example, leaving the partial melt produced relatively depleted in this element. Similarly, a partial melt that was in equilibrium with residual plagioclase will be relatively depleted in Sr.

2 Once a mineral has melted, it can no longer influence the chemical composition of the liquid.

3 Perhaps most important, partial-melting processes are likely to be extremely complex and the best we can do is to set up a model which might approximate to the real situation. In practice, the first tiny drops of melt will consist of the low-temperature minerals (such as plagioclase) and they will tend to form a thin film along the grain boundaries. Once this film is just several layers of atoms thick, elements can start to migrate, first by diffusion (which we discussed in Section 4.2) and later by *convection*[A]. At a very early stage, liquid may become separated physically from the minerals with which it was first in equilibrium, and, as the degree of melting increases, globules of liquid may form and migrate together. Eventually, therefore, the structure of the original rock will be destroyed as residual minerals become separated and move freely in the melt.

Many models have been used to describe the behaviour of trace elements during partial melting, but we shall consider just one—it illustrates principles that are basic to more complex models and it would appear to represent a reasonable approximation of what may happen in nature. If the melt remains in equilibrium with the residual minerals until the two are separated physically (perhaps by removal of the melt), the concentration of a trace element in the melt may be given by the equation

$$C_1 = \frac{C_o}{D + F(1 - D)} \qquad (4)$$

where C_1 = the concentration of the trace element in the liquid, C_o = the initial concentration of the trace element in the solid before melting commenced, D = the *bulk partition coefficient* for the trace element distributed between all the minerals present and the partial melt, and F = the degree of melting expressed as a fraction between 0 and 1 (thus a 10 per cent partial melt is written as $F = 0.1$).

bulk partition coefficient, D

The *bulk* partition coefficient (D) reflects the fact that a trace element will be present in different amounts in the different minerals in a rock: it therefore takes into account both the proportions of the minerals in the original rock and the individual partition coefficients (K_D) for each mineral.

Thus for a particular trace element,

$$D = (X_o K_D)_\alpha + (X_o K_D)_\beta + (X_o K_D)_\gamma + \cdots \qquad (5)$$

where α, β and γ are the different minerals and X_o and K_D are respectively the proportions of the minerals in the original rock and the partition coefficients for the trace elements in each mineral.

As an example, consider a solid sample consisting of 65 per cent anorthite and 35 per cent diopside in the system anorthite–diopside (as in Figure 13, p. 21). Those percentages are the proportions of these two minerals in the original rock and when expressed between 0 and 1,

$$X_{o\,\text{anorthite}} = 0.65$$
$$X_{o\,\text{diopside}} = 0.35$$

When this sample is heated, the distribution of, say, rubidium (Rb) between the residual crystals of anorthite and diopside and the liquid is expressed, using the partition coefficients for rubidium for the individual minerals. For this example we shall use K_D values for plagioclase (0.07) and clinopyroxene (0.001) from Table 8.

Then if α = anorthite and β = diopside, the bulk partition coefficients for Rb can be calculated:

$$D = (X_o K_D)_\alpha + (X_o K_D)_\beta$$
$$= (0.65 \times 0.07) + (0.35 \times 0.001)$$
$$= 0.0459$$

If we know the concentration of Rb in the original solid (C_o) we may now calculate what it will be in the liquid (C_1) for different degrees of partial melting (F) of our

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sample of 65 per cent anorthite and 35 per cent diopside. If there was 10 p.p.m. Rb in the original solid and $D = 0.0459$ (as above), after 10 per cent partial melting ($F = 0.1$), C_1 is given by equation 4:

$$C_1 = \frac{C_o}{D + F(1 - D)}$$

$$= \frac{10}{0.0459 + 0.1(1 - 0.0459)}$$

$$= \frac{10}{0.0459 + 0.09541}$$

$$= 70.7 \text{ p.p.m.}$$

After 10 per cent partial melting, the concentration of Rb in the liquid is 70.7 p.p.m.

> **ITQ 25** For this same sample with 65 per cent anorthite and 35 per cent diopside and containing 10 p.p.m. Rb, calculate the concentration of Rb in the liquid (C_1) after 25 per cent partial melting, that is, $F = 0.25$. (Use $D = 0.0459$, as calculated above.)

Note that the answer to ITQ 25 indicates that after 25 per cent partial melting the concentration of Rb in the liquid was approximately *half* what it was after 10 per cent melting.

> Can you suggest why that might be?

Rubidium is an incompatible element; it tends to reside in the liquid and its concentration is greatest in small initial melts. As the amount of melting increases the concentration of rubidium is simply diluted by the increasing volume of liquid.

This model to describe the distribution of trace elements during partial melting is clearly an over-simplification—an approximation of what may actually take place in nature. Without dwelling on this point, there is one concept, not incorporated in the model, that we should always bear in mind; namely, that *the proportions of minerals actually entering a melt are usually different from those in the original rock*— simply because some minerals melt at lower temperatures than others (see Section 1). More sophisticated models are required to cope with these effects but they are beyond the scope of this Course.

We have seen how to use our model to calculate the concentration of a trace element in a liquid after a specific amount of partial melting. We may now broaden the discussion to consider (i) how the concentration of a trace element in the liquid changes *as* the amount of melting changes, and (ii) how concentrations of trace elements in a liquid vary depending on the size of the bulk partition coefficient D.

The sample consisting of 65 per cent anorthite and 35 per cent diopside contains 10 p.p.m. of both Rb and Sr. Figure 48 uses the answer to ITQ 25 to plot the concentration of Rb in the liquid between zero and 25 per cent partial melting. Significantly, for a sample of this composition (65 per cent An, 35 per cent Di) the liquid remains at the eutectic point (that is, both An and Di melt together) until 50 per cent of the sample has melted. Thus all the variations in Rb content portrayed in Figure 48 are in liquids of the *same major-element composition*—they reflect different degrees of melting *at the eutectic point* (E in Figure 13).
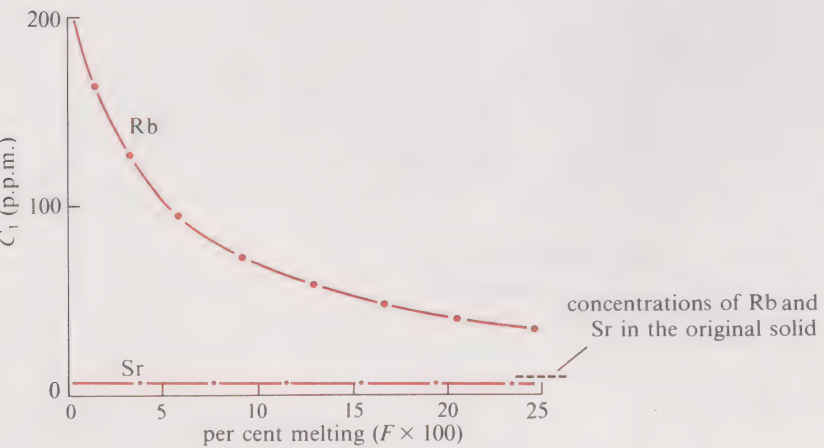

FIGURE 48   Rb and Sr concentrations in the liquid (C_1) after 0–25 per cent partial melting of a sample of 35 per cent Di, 65 per cent An.

Secondly, the shape of the curve in Figure 48 indicates that the rubidium content of the liquid is extremely sensitive to the amount of melting that has taken place. It follows, therefore, that, if we wish to assess how much partial melting a particular sample represents, we shall learn more from trace elements such as rubidium than from major elements which, at least in this example, do not change until the degree of melting is more than 50 per cent.

Thirdly, the bulk partition coefficient for rubidium in this system is small (D = 0.045 9), and the variation of the concentration of Rb in the liquid with the per cent melting in Figure 48 is typical of an incompatible element. It is very difficult for such elements to find sites in the structures of the available minerals during crystallization and thus on melting they tend to migrate into the first drops of liquid to form. Further melting then merely dilutes the concentration of the incompatible element in the liquid, and thus, in our example, the Rb content of the liquid decreases fairly rapidly as the amount of melting increases (Figure 48 and ITQ 25).

Let us now compare the behaviour of rubidium with that of strontium during partial melting of this sample with 65 per cent anorthite and 35 per cent diopside. Look at the partition coefficients for Sr distributed between clinopyroxene and plagioclase, and a basaltic liquid in Table 8.

> Would you expect the *bulk* partition coefficient (D) for Sr in our sample of 65 per cent An and 35 per cent Di to be larger or smaller than that for Rb?

Since the individual partition coefficients for Sr are larger than those for Rb in both clinopyroxene and plagioclase, the bulk partition coefficient for Sr in our sample must also be larger than that for Rb.

> Hence, will the concentration of Sr in the liquid be higher or lower than that of Rb, at the same degree of partial melting?

Because the bulk partition coefficient for Sr is higher than that for Rb, the concentration of Sr in the crystals will be higher; thus the concentration of Sr in the liquid will be lower after any given amount of melting.

Check that you understand these deductions by answering ITQ 26.

> **ITQ 26** (a) Calculate the bulk partition coefficient D for Sr in our sample with 65 per cent anorthite and 35 per cent diopside. Take the values of the individual partition coefficients from Table 8 as before: 2.2 for anorthite; 0.07 for diopside.
>
> (b) Use your result from (a) and equation 4 for partial melting to calculate the concentration of Sr in the liquid after 15 per cent partial melting. Remember that the original sample contained 10 p.p.m. Sr.

The answer to ITQ 26 is also plotted in Figure 48, which illustrates how the concentration of Sr in the liquid varies with different amounts of partial melting of this sample of 65 per cent anorthite and 35 per cent diopside. Sr is a compatible element in this system (the bulk partition coefficient is greater than one; $D = 1.46$, as you know from the answer to ITQ 26) and therefore the concentration in the liquid is *less* than that in the original solid—Sr tends to remain in the crystals, particularly in those of anorthite which have not yet melted.

You should recall from the discussion of fractional crystallization that, if a partition coefficient *equals* one, then the concentration of the element in the solid is the same as that in the liquid and *neither* changes during fractionation. Similarly, for partial melting, if the partition coefficient equals one, then the concentrations of the element in the liquid and the solid remain the same. Thus, because the bulk partition coefficient for Sr in our example is fairly close to one ($D = 1.46$), the Sr content in the liquid changes only very slowly as the amount of melting increases. This results in the virtually horizontal line in Figure 48, which contrasts so sharply with the variation of an incompatible element like Rb.

In summary, the trace-element variations in liquids that represent different degrees of partial melting enable us to study the evolution of such liquids in much finer detail than is possible using major elements. In the example we considered (65 per cent An, 35 per cent Di), it was possible to study relationships between liquids whose major-element compositions were *identical* (because they were all eutectic liquids). Let us now look at the partial melting of a natural rock, peridotite.

7.4 Partial melting of upper mantle peridotite

Peridotite is the name given to the many olivine-rich rock types in the upper mantle, and since that is the source of at least the basic magmas erupted on the Earth's surface it is of prime concern to most geologists. As discussed in Block 2, peridotite consists predominantly of olivine, with lesser amounts of ortho- and clinopyroxene and an aluminous mineral (plagioclase feldspar, spinel or garnet). In this Section we shall apply our partial-melting model to the melting of peridotite, primarily to illustrate some general principles of how trace elements behave during partial melting and also to assess how much may be deduced about the trace-element geochemistry of a source rock (peridotite) from that of a partial melt (basalt).

Fragments of the upper mantle are sometimes brought up to the surface (e.g. in kimberlite pipes, *CB*, Plate 32) and, as discussed in Block 2, Section 4.2.2, we know from them that a piece of 'typical' peridotite might consist of 60 per cent olivine, 18 per cent orthopyroxene, 12 per cent garnet and 10 per cent clinopyroxene.

Using the partition coefficients for individual minerals from Table 8, we may therefore calculate bulk partition coefficients (*D*) for different trace elements distributed between this peridotite and a basaltic melt. Values of *D* for Rb, Sr, Ba, Zr and Y are listed in Table 9.

TABLE 9   Calculated bulk partition coefficients (*D*) for selected trace elements during the partial melting of peridotite (60 per cent olivine, 18 per cent orthopyroxene, 12 per cent garnet and 10 per cent clinopyroxene), using the K_D values in Table 8.

Rb	Sr	Ba	Zr	Y
0.001	0.010	0.001	0.057	0.332

You should now be sufficiently familiar with partition coefficients to see that all the trace elements in Table 9 are incompatible; *D* is less than one and thus during melting these trace elements are concentrated in the liquid. For this peridotite, Rb and Ba have the lowest values of *D* and they will be most enriched in the liquid, while for Y the value of *D* is relatively large and thus its concentration in the liquid will not be much greater than that in the original solid.

If you look back at Table 8, can you suggest why *D* for yttrium (Y) in Table 9 is significantly larger than those for the other elements?

The garnet in the peridotite preferentially retains Y; for garnet the K_D for yttrium = 2.0 (Table 8).

We may now consider what happens to two trace elements, rubidium and strontium, during partial melting of peridotite. Although these elements are both incompatible, their bulk distribution coefficients differ by a factor of ten (Table 9). Average mantle peridotite contains about 0.8 p.p.m. Rb and 25 p.p.m. Sr. Using these figures and equation 4 (Section 7.3), we can calculate the Rb and Sr contents of the melt after different degrees of partial melting. The results are presented graphically in Figure 49.

ITQ 27   Look at Figure 49.

(a)   Are Rb and Sr concentrated in the liquid, or do they tend to remain in the solid?

(b)   What are the concentrations of Rb and Sr in the liquid after 5 per cent partial melting compared with those in the original solid (0.8 p.p.m. Rb and 25 p.p.m. Sr)?

(c)   How does the Rb/Sr ratio in the liquid compare with that in the original solid after 10 per cent partial melting?

Your answers to ITQ 27 illustrate variations entirely typical of two incompatible elements during partial melting. Both are strongly concentrated in the liquid. A 5 per cent melt contains almost 16 p.p.m. Rb and over 400 p.p.m. Sr—concentrations that are twenty times greater than those in the original peridotite—and, even after 20 per cent melting, the concentrations in the melt are still 5 times greater than those in the original solid.
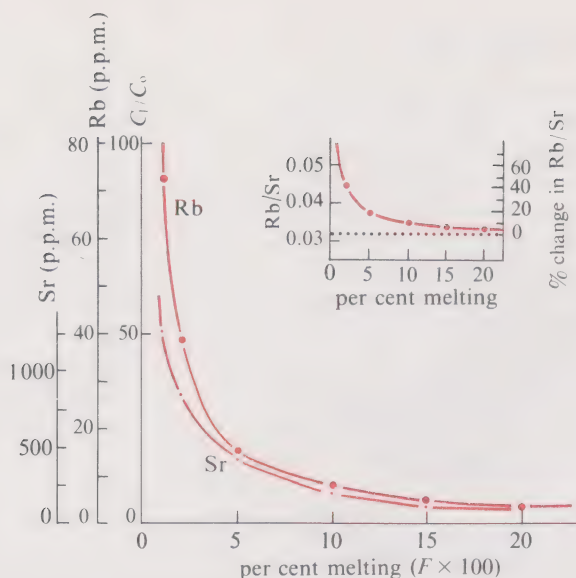
FIGURE 49 Relative enrichment (C_1/C_o) of Rb and Sr in the liquid for 0–20 per cent partial melting of garnet peridotite. *Inset* Variation of Rb/Sr ratio in the liquid during increasing partial melting (red line) compared with that in the original peridotite (black dotted line).

These large variations in the concentrations of the incompatible elements in the liquid are in sharp contrast to the way in which the *ratio* of Rb to Sr changes during partial melting. D for Rb is less than that for Sr (Table 9) and consequently Rb is *relatively* more enriched in the liquid after small amounts of partial melting than Sr. Thus, at small degrees of partial melting (less than 5 per cent, Figure 49), the Rb/Sr ratio of the liquid is significantly higher than that in the solid; however, as the amount of partial melting increases, the curves for Rb and Sr in Figure 49 soon coalesce. Thus we may predict that, once more than about 5 per cent partial melting has occurred, the ratio of Rb/Sr should not vary significantly with the amount of partial melting. This is illustrated in the inset to Figure 49. After 10 per cent partial melting of this peridotite, the Rb/Sr ratio in the melt is 0.035 (ITQ 27)—only 0.003 higher than that in the original peridotite.

Thus we have arrived at two extremely important conclusions that apply to all elements with small bulk partition coefficients.

1 After 5–10 per cent partial melting, the *ratio* of two incompatible elements in a melt changes very little as the amount of melting increases.

2 After about 10 per cent partial melting, the *ratio* of two incompatible elements in a melt is therefore similar to that in their original source rock.

Moreover, these conclusions hold true even when the two trace elements in question have very different values of *D*—those for Rb and Sr differed by a factor of ten.

Let us now combine these conclusions with those we deduced about the behaviour of trace elements during fractional crystallization.

The ratio of the concentrations of two incompatible elements in a *liquid* is not changed significantly by fractional crystallization (Section 7.1), so we can estimate the *ratio* of such elements in an original magma from the ratio in rock types derived from it.

Similarly, after 5–10 per cent partial melting, the ratio of two incompatible elements in the melt will be close to that in the original source rock. Thus, provided our original (or primary) magma represents more than 5–10 per cent partial melting, we may estimate *the ratio of two incompatible elements in a source rock* from the ratios determined in even quite evolved volcanic rocks, given that they represent liquids.

Moreover, because incompatible element abundances are very sensitive to how much partial melting and fractional crystallization has taken place, it follows that we cannot estimate the *concentrations* of incompatible trace elements in a source rock with nearly as much confidence as we can estimate the *ratio* of concentrations of such elements.

Thus, by considering the ratios of incompatible elements, we may assess whether or not different igneous rocks could have been derived from source rocks with similar trace-element compositions. For example, much of the ocean floor consists of basalt which is generated along ocean ridges, and basalt is also erupted on islands away from ocean ridges. Moreover, in general the 'ocean-island' basalts tend to have higher concentrations of incompatible elements (K, Rb, Sr, and so on) than the 'ocean-ridge' basalts.

Can you suggest two possible causes of the higher concentrations of incompatible elements in ocean-island basalts?

Looking at Figure 49 and the variation of Rb and Sr in the liquid at different degrees of partial melting, you should see that differences in the concentrations of incompatible elements in these oceanic basalts might reflect (i) different degrees of partial melting and/or (ii) different concentrations of incompatible elements in their source rocks. Since we have argued that *ratios* of incompatible elements are affected very much less than their actual concentrations by differences in the amount of melting, we should be able to distinguish between those two possibilities by considering the differences in ratios of incompatible elements. You can try that for yourself by answering ITQ 28.

ITQ 28 Ocean-ridge basalts have Rb/Sr ratios of about 0.01, whereas many of those on ocean islands have Rb/Sr ratios of about 0.06.

(a) Using the graph showing the Rb/Sr ratio in the liquid as a percentage of that in the original solid in Figure 49, estimate the Rb/Sr ratio in a 2 per cent melt of a source rock with an Rb/Sr ratio of 0.01.

(b) Assuming that all basalts represent more than 2 per cent melting of peridotite, could ocean-island and ocean-ridge basalts be derived by partial melting of peridotite with the same Rb/Sr ratio?

From the answer to ITQ 28 we must conclude that basalts erupted along ocean ridges and on oceanic islands are not derived from peridotite with the same trace-element geochemistry; that is, *significant chemical variations exist within the upper mantle*. This, in its turn, raises other questions to which we shall return later in this Course. How were these chemical variations generated? How long have they been there? How do they survive at all if the mantle is continuously convecting beneath the moving plates that make up the Earth's crust?

7.5 Summary of Section 7

(a) In contrast with major elements, trace elements rarely, if ever, form minerals of their own. They have little or no influence over which minerals are going to crystallize; rather their distribution reflects the minerals that were present during melting or crystallization and the difficulty they had finding sites in those minerals.

(b) The distribution of a trace element between two phases is described in terms of a partition coefficient (K_D), and for mineral/liquid equilibria this is conventionally less than one if the trace element is concentrated in the liquid. Such trace elements are often termed *incompatible*, while those with partition coefficients greater than one are called *compatible*.

(c) The ease with which an element can substitute into a particular mineral is controlled largely by how the *size* and the *charge* of the substituting ion compare with those of the major elements in the crystal lattice. When the size and charge of both are similar, the trace element will tend to be preferentially incorporated into that mineral and its partition coefficient will thus be greater than one. For example, Sr^{2+} (112 pm) replaces Ca^{2+} (99 pm) in plagioclase feldspar, and its partition coefficient for plagioclase in equilibrium with basaltic magma is 2.2 (Table 8).

(d) Simple models were devised to describe the behaviour of trace elements during fractional crystallization and partial melting. The majority of trace elements are *incompatible* in basic magmas and thus tend to be concentrated in the liquid. Their concentrations in the liquid are very sensitive to the amount of crystallization or partial melting that has taken place.

(e)   The *ratio* of two *incompatible* elements is insensitive to the degree of both partial melting and fractional crystallization. Thus we may estimate such ratios in primary magmas, and hence in their source rocks, from the ratios determined in at least basic to intermediate volcanic rocks.

(f)   Because high partition coefficients are uncommon, when they do occur they are diagnostic of a particular mineral; for example, unusually low concentrations of Sr in igneous rocks are often an indication that they have been in equilibrium with plagioclase feldspar.

7.6   Objectives for Section 7

Now that you have completed Section 7, you should be able to:

1   Define in your own words, and recognize formal definitions of, the terms flagged in the margins of this Section.

24   Calculate partition coefficients and use them to predict qualitatively how a particular trace element is distributed between co-existing crystals and liquid.

25   Calculate what happens to the concentrations of trace elements in a magma during fractional crystallization of different minerals.

26   Explain in your own words the factors that control whether a trace element will be able to substitute readily into a particular mineral.

27   Calculate *bulk* partition coefficients for a rock containing two or more minerals.

28   Use a simple model for partial melting to calculate the distribution of different trace elements at different degrees of partial melting.

29   Use the ratios of incompatible trace elements in igneous rocks to estimate those in their primary magmas, and hence in their original source rocks.

Apart from Objective 1, to which they all relate, the seven ITQs in this Section test these Objectives as follows: ITQ 22: Objective 25; ITQ 23: Objective 24; ITQ 24: Objective 25; ITQ 25: Objective 28; ITQ 26: Objectives 27 and 28; ITQ 27: Objective 29; ITQ 28: Objective 29.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 21 (*Objectives 24 and 25*)   (a)   A phenocryst of plagioclase feldspar containing 225 p.p.m. strontium (Sr) occurs in a groundmass which has 100 p.p.m. Sr. Calculate the partition coefficient (K_D) for Sr distributed between that plagioclase and the co-existing liquid.

(b)   Calculate how much of that plagioclase must crystallize to reduce the concentration of Sr in the liquid from 100 to 75 p.p.m.

SAQ 22 (*Objectives 27 and 29*)   (a)   Using the partition coefficients for individual minerals in Table 8, calculate the *bulk* partition coefficient (*D*) for potassium (K) distributed between peridotite (60 per cent olivine, 18 per cent orthopyroxene, 12 per cent garnet, 10 per cent clinopyroxene) and a basaltic melt.

(b)   The bulk partition coefficient for zirconium (Zr) distributed between the same peridotite and a basaltic melt is 0.057 (Table 9). Will the Zr/K ratio of a 10 per cent melt be slightly *higher* or *lower* than that in the original peridotite?

SAQ 23 (*Objectives 28 and 29*)   Zirconium (Zr) and yttrium (Y) are two elements widely used in the study of igneous rocks.

(a)   Use equation 4 to calculate the Zr/Y ratios in magmas produced after 5 per cent and 15 per cent melting of garnet-bearing peridotite. Use the bulk partition coefficients in Table 9, and assume that the original peridotite contains 8 p.p.m. Zr, and 4 p.p.m. Y.

(b)   Figure 50 is a histogram of Zr/Y ratios determined on geologically young basalts erupted in oceanic areas. Use your results from (a) to interpret these data. Could ocean-island and ocean-ridge basalts be derived by different degrees of partial melting of garnet-bearing peridotite? Under what conditions might these two groups of basalt be derived by partial melting of peridotites with the same Zr/Y ratio?
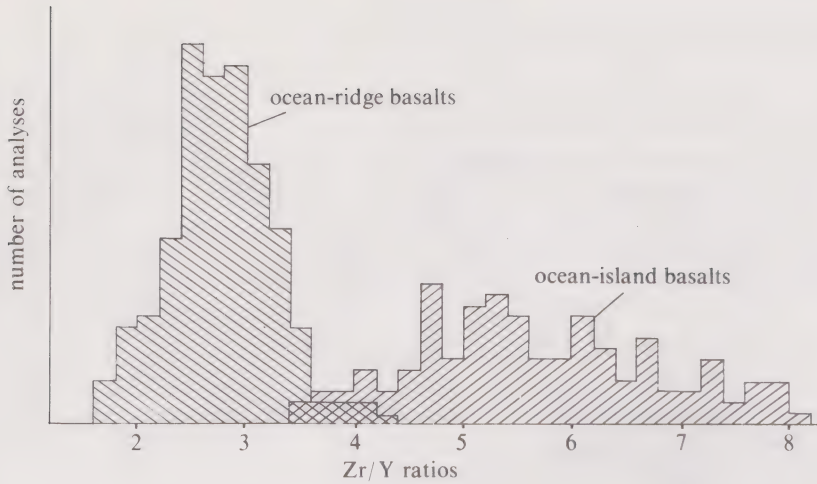
SAQ 24 (*Objectives 28 and 29*)   Two basalts contain 1 p.p.m. Rb and 100 p.p.m. Sr and 11 p.p.m. Rb and 80 p.p.m. Sr respectively.

(a)   Calculate their Rb/Sr ratios and decide which is more likely to have been derived by partial melting of plagioclase-bearing peridotite.

(b)   If the basalt you chose in (a) represents 15 per cent partial melting, calculate the Rb/Sr ratio in the original plagioclase-bearing peridotite. Assume that the bulk partition coefficients (D) for Rb and Sr are 0.085 and 0.272 respectively.

8   Strontium isotopes—some geological applications

Many elements contain more than one kind of atom. Atoms of the same element which have different masses are called *isotopes*[A]. Some isotopes are unstable—they *decay* and in so doing emit radiation. This is the process of *radioactive decay*[A]. It is responsible for much of the heat within the Earth (which will be discussed in Block 4) and it has been harnessed by geologists both as an isotopic time-piece to date events throughout most of Earth history and as a sensitive tool for the study of chemical evolution.

Materials that contain a radioactive isotope have a built-in 'clock' for measuring their age. The principle is very simple. The rates of decay of all the common radioactive isotopes are constant and may be determined by accurate laboratory measurements on pure samples. If the amounts of a radioactive isotope present both when the material was formed and today are known, then the age of the material may be calculated using the known decay rate for that isotope. In your Science Foundation Course this was illustrated using the decay of ^{14}C, ^{235}U and ^{238}U. In this Section we shall revise briefly the principles of radioactive decay and show how they may be applied to the dating of rocks and minerals, and then concentrate on two elements which we have already discussed in some detail—rubidium (Rb) and strontium (Sr).

8.1   Radioactivity applied to dating

The basic *law of radioactive decay* states very simply that the rate at which the numbers of radioactive atoms decrease is proportional to the number of atoms present. The rate of decay is *exponential*[A].

law of radioactive decay

You met exponential processes in your Science Foundation Course, for example when considering the growth of potential organisms. If a population doubles in size in each generation, then after n generations the number of offspring (M) is given by

$$M = 2^n \tag{6}$$

With radioactive decay, however, the parent atoms are decaying (and emitting radiation) and thus their numbers *decrease* exponentially with time. If P_o is the number of original parent atoms and the number of those surviving after any particular length of time is called P, the decay process may be written in a similar way

$$P = P_o \times (\tfrac{1}{2})^n \tag{7}$$

where n is the number of *half-lives*[A] ($T_{\frac{1}{2}}$) of the decay scheme concerned, the half-life being the time taken for half the material present at any given time to decay.

Figure 51 illustrates how the number of parent atoms (P) decreases with time. Note that, as we stated above in equation 7, the rate at which P decreases depends on the number which were present. Thus when P is 10 it is reduced by 5 in the next unit of time, and yet when P is 2 it is reduced by only 1 in the *same* length of time. This is the nature of an *exponential* decay process. We may also assume that the decay of *one* radioactive parent atom produces *one* daughter atom, thus as illustrated in Figure 51, the number of daughter atoms produced by radioactive decay increases as rapidly as the number of parent atoms decreases.
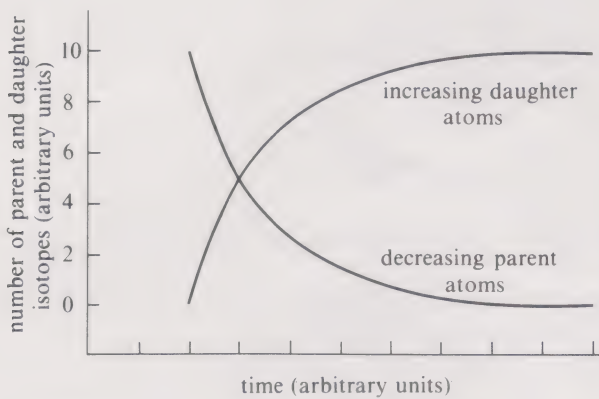
FIGURE 51   The changing number of parent and daughter atoms during radioactive decay. Note that growth in the number of daughter atoms (D^*) is the mirror image of the decay curve of the number of parent atoms.

It can be shown that if a number of parent atoms P decays to daughter atoms D^* over a period of time t, then

$$D^* = P(e^{\lambda t} - 1) \tag{8}$$

where e to a power, e.g. e^2, e^3 or $e^{\lambda t}$ is simply a mathematical term describing an exponential curve, and λ is a constant, termed the *decay constant*, which has a characteristic value for each radioactive isotope. It represents the probability that a single atom will decay within a given length of time. Moreover, it is a relatively simple matter to relate it to the *half-life* of such an element. The half-life, $T_{\frac{1}{2}}$, is the time taken for half a radioactive sample to decay—whereupon the sample will consist of equal amounts of the parent atoms P and the daughter atoms D^*, produced by decay of P. So, if we put D^* and P both equal to one in equation 8 we get:

decay constant

$$1 = (e^{\lambda T_{\frac{1}{2}}} - 1) \tag{9}$$

or $\qquad\qquad e^{\lambda T_{\frac{1}{2}}} = 2$

Then, since to remove e we must take logarithms to the base e (written ln),

$$\lambda T_{\frac{1}{2}} = \ln 2, \text{ or } 0.693 \tag{10}$$

Thus, the half-life, $\qquad\qquad T_{\frac{1}{2}} = \dfrac{0.693}{\lambda} \tag{11}$

Here we may simplify equation 8 by making an approximation. Providing that λt is a small number, which it is for most of the radioactive decay schemes used in geology, $(e^{\lambda t} - 1)$ is approximately equal to λt.

Thus we may rewrite equation 8 in an approximate form:

$$D^* = P\lambda t \tag{12}$$

We stated that, in this equation, D^* is the number of daughter atoms produced by the decay of parent atoms *over a period of time t*. However, if we determine the total number of daughter atoms (D) in any sample at the present time, only some of them will have been produced during the time period that we are trying to date—some will have been present before.

Thus, the total number of daughter atoms (D) consists of those produced by radioactive decay during the period of time t (D^*), plus those already present at the time of formation (D_o); that is $D = D_o + D^*$.

Since $D^* = P\lambda t$ (equation 12),

$$D = D_o + P\lambda t \qquad (13)$$

And this is the general equation used to calculate the ages of rocks and minerals from radioactive decay schemes. Note that geological ages are expressed in numbers of years *before present*. Hence the time of formation of a sample is numerically the same as its age—a rock formed at 500 Ma is clearly 500 Ma old!

8.2 The dating of rocks and minerals by Rb–Sr

Rubidium occurs in two isotopic forms, the *present-day* relative abundance of which are:

$$^{87}_{37}Rb \qquad 27.85 \text{ per cent}$$

$$^{85}_{37}Rb \qquad 72.15 \text{ per cent}$$

One of the isotopes ($^{87}_{37}Rb$) is unstable and decays by β-radiation (effectively the transformation of a neutron to a proton plus an electron which is expelled as a negatively charged particle or β-particle[A]) to produce a stable isotope of strontium:

$$^{87}_{37}Rb \xrightarrow{\beta\text{-particle decay}} {}^{87}_{38}Sr$$
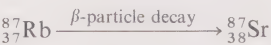
Strontium has four natural isotopes and they are all stable; their present-day relative abundances in a typical terrestrial sample are

$^{88}_{38}Sr \qquad 82.61 \text{ per cent}$

$^{87}_{38}Sr \qquad 6.96 \text{ per cent (stable, but } augmented \text{ by decay of } ^{87}_{37}Rb)$

$^{86}_{38}Sr \qquad 9.88 \text{ per cent}$

$^{84}_{38}Sr \qquad 0.55 \text{ per cent}$

The decay of radioactive $^{87}_{37}Rb$ to stable $^{87}_{38}Sr$ clearly results in changes in the isotopic composition of Rb and Sr. Isotopes are measured by *mass spectrometry*[A] as shown on TV 07, and since mass spectrometers measure *ratios* of isotopes, isotope composition is expressed as a ratio of two isotopes, for example $^{87}Sr/^{86}Sr$. (Note that it is conventional not to include the atomic number every time when writing these isotopes.)

> ITQ 29 (a) With the passage of time, will the following ratios in a sample containing both rubidium and strontium increase, decrease, or remain unchanged?
>
> (i) $^{87}Rb/^{85}Rb$; (ii) $^{87}Sr/^{86}Sr$; (iii) $^{86}Sr/^{84}Sr$.
> (b) In a rock that contains no Rb at all, will the $^{87}Sr/^{86}Sr$ ratio increase, decrease, or remain unchanged with the passage of time?
> (c) In a rock that initially contains no Sr at all, will the $^{87}Rb/^{85}Rb$ ratio increase, decrease, or remain unchanged with the passage of time?

Since almost all rocks and minerals contain at least small amounts of Rb and Sr, you can now see why the isotope abundances given at the beginning of this Section were for present-day Rb and Sr.

Clearly, with time, the $^{87}Sr/^{86}Sr$ ratio of a rock will increase and its $^{87}Rb/^{86}Sr$ ratio will decrease, because of the production of ^{87}Sr from ^{87}Rb. The degree of enrichment of ^{87}Sr in a rock therefore depends upon (a) how old it is, and (b) the amount of rubidium relative to strontium that it contains, that is, its Rb/Sr ratio.

> But to determine the age of a rock or mineral, what do we measure and how do we calculate the result?

Consider our general equation for radioactive decay (equation 13),

$$D = D_o + P\lambda t$$

For Rb and Sr, ^{87}Rb decays to ^{87}Sr, and thus ^{87}Rb is the parent atom and ^{87}Sr is the daughter atom, consisting of some atoms produced by radioactive decay during the period of time t we are trying to date ($^{87}Sr^*$) and some ($^{87}Sr_o$) that were already present at the time of formation of our sample—let us call it t_o.

Substituting in equation 13, we get

$$^{87}\mathrm{Sr} = {}^{87}\mathrm{Sr_o} + {}^{87}\mathrm{Rb}\lambda t$$

However, as mentioned above, mass spectrometers determine *ratios* of isotopes and thus it is convenient to divide this equation across by a stable isotope that is not involved in the decay scheme, in this case $^{86}\mathrm{Sr}$.

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right) = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_o + \left(\frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}\right)\lambda t \qquad (14)$$

The present-day Sr-isotope composition $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ can be determined by a mass spectrometer and the $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ ratio can be calculated once the present-day concentrations of Rb and Sr have been determined—usually by *X-ray fluorescence*[A]. Assuming that the decay constant λ has already been measured experimentally, then we may calculate the period of time t (the age before present) once we have estimated the Sr-isotope composition of our sample at the time of its formation, $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$.

At first glance, that may seem rather a tall order. Most rocks are many millions of years old and clearly none of us was around at the time (t_o) when they were formed to measure the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio of the sample at that time—even if a mass spectrometer had been available! However, if we re-arrange equation 14, then

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right) = \left(\frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}\right)\lambda t + \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_o \qquad (15)$$

This equation is in the form $y = mx + c$. In other words it is the equation of a *straight line*[A].

For samples of the same age and $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$, a graph of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ against $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ should be a straight line with a slope of λt and an intercept corresponding to $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$. Note also that since $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_o$ is the Sr-isotope ratio at the time of formation t_o, it is usually referred to as the *initial Sr-isotope ratio*.

initial Sr-isotope ratio

How many points do you need to draw a straight line?

You need at least *two* points—but note that since this straight line is being determined experimentally, the more points you have the better.

You should also note that since this straight line is being drawn on a diagram of $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ against $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$, the points representing the samples analysed must have *different* $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ and consequently different $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios. In practice, Rb/Sr ratios are determined first, and samples with different Rb/Sr ratios are then selected for Sr-isotope analysis.

As an example, let us consider just four samples from a hypothetical suite of volcanic rocks that were erupted during the same volcanic event t million years ago. These rocks were selected because (a) they have different Rb/Sr ratios, and (b) they are believed to have been derived from the *same* primary magma (by fractional crystallization of varying amounts of plagioclase and clinopyroxene, as for example in Section 7.1). This is significant because we may assume that rocks derived from the same magma will, at the time of their formation, t_o, have had the same $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio, that of the primary magma.

When the rocks formed, therefore, the processes of fractional crystallization ensured first that the *trace-element ratio Rb/Sr* would be *different* in these rocks; and second that the *isotope ratio $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$* would be the *same*.

We can represent that graphically, as in Figure 52, which is a graph of $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ against $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$. The line AB on that graph represents the situation at time t_o when the rocks formed: the $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ ratios are all different, but the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios are all the same.

The sloping line AC represents the situation today: the $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ ratios are still different, but now so are the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios.

What has happened?
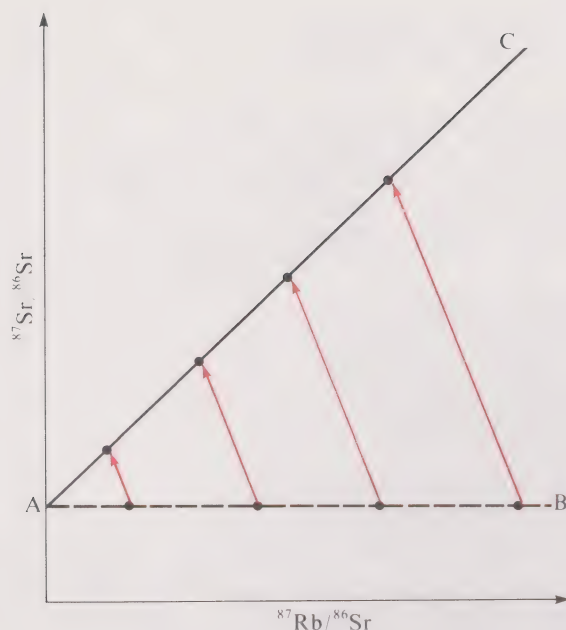
FIGURE 52 A graph of $^{87}Sr/^{86}Sr$ against $^{87}Rb/^{86}Sr$ (an isochron diagram) illustrating how four samples of the same age but different Rb/Sr ratios evolve from a horizontal line (AB) at the time of their formation, to plot on a straight line (AC) whose slope equals λt at the present time.

^{87}Rb has decayed to ^{87}Sr over the time period t from the formation of these rocks (at t_o) to the present day; and that has had two effects:

(i)   it has *reduced* the amount of ^{87}Rb present, and so the $^{87}Rb/^{86}Sr$ ratios have decreased slightly;

(ii)   it has increased the amount of ^{87}Sr, and so the $^{87}Sr/^{86}Sr$ ratios have increased.

> But why have the $^{87}Sr/^{86}Sr$ ratios increased by different amounts along the line AC?

The amount of ^{87}Sr produced by radioactive decay depends on the amount of ^{87}Rb present. However, on Figure 52 we have plotted isotope ratios: hence the *relative* increase in ^{87}Sr (the increase in $^{87}Sr/^{86}Sr$) depends on the *relative* amount of ^{87}Rb (on the ratio $^{87}Rb/^{86}Sr$). After a given period of time, the samples with the highest $^{87}Rb/^{86}Sr$ ratios will also be those that generate the highest $^{87}Sr/^{86}Sr$ ratios by radioactive decay.

Now, look back to equation 15 and recall that it is an equation for a straight line. As in Figure 52, a graph of $^{87}Rb/^{86}Sr$ against $^{87}Sr/^{86}Sr$ gives a straight line whose slope is equal to λt, where t is the time since the formation of a sample, that is, its age.

> Will older samples lie on lines with steeper or shallower slopes on diagrams such as Figure 52?

Clearly, the steeper the slope, the larger the value of t, and hence the older the samples. The line AB in Figure 52 has zero slope and so t is zero, which is what we said at the beginning—the line AB represents the situation when the rocks first formed. The line AC represents the situation at the present day when the rocks are t million years old. And in the future, when t increases as the rocks become older, the slope will increase further. Can you see, therefore, that groups of rocks with *different* ages give different slopes and can be dated using this method?

The straight lines AB and AC on Figure 52 connect samples *of the same age* and they are therefore called *isochrons*. The diagram of $^{87}Sr/^{86}Sr$ versus $^{87}Rb/^{86}Sr$ is an *isochron diagram*. The line AB is an isochron corresponding to an age of zero, while AC corresponds to an age of t million years.

isochron
isochron diagram

The samples in Figure 52 represent an idealized case, but in describing their evolution and the formation of the isochron AC we made several extremely important assumptions. They apply in general to all dating systems and you have already met them, albeit in a different form, in the discussion of *uranium–lead* (*U–Pb*) *dating*[A] in your Science Foundation Course Nonetheless, they are worthy of further emphasis.

If we are to date samples by radioactive decay and if in particular they are to plot on an isochron whose slope really reflects their true age, then the following assumptions must be upheld:

1 All the samples we analyse must be of the same age. This would seem to be obvious, and when, for example, the samples are collected from the same igneous intrusion then clearly it is a reasonable assumption. However, if we collected samples over a large area where the geology was still poorly understood we might well collect samples of different ages without realizing it. In such a case, the isotope ratios we measured would *not* plot on a straight line.

2 All the samples must have the same initial Sr-isotope ratio, $(^{87}Sr/^{86}Sr)_o$, otherwise they will not plot on the same straight line on an isochron diagram like Figure 52, either when they are formed (at time t_o) or at the present day (after t million years). It is most likely in a suite of igneous rocks thought to have crystallized from similar liquids; it is least likely in sediments composed as they often are of different fragments of pre-existing material.

3 The third assumption is that between the formation of the samples and the present day the $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios have changed *only* by the process of radioactive decay; no Rb or Sr has been added to, or lost from, the system.

In practice, if any of these assumptions is not valid for a suite of samples then the results will tend to scatter when plotted on an isochron diagram. Conversely, therefore, if all the results do plot on, or close to, a single straight line (for example, line AC in Figure 52) it is probable that the assumptions have been upheld and that the samples really were formed at the calculated time t million years ago.

Let us now see how these assumptions, and the whole method of determining ages from a suite of samples plotted on an isochron diagram, may be applied to a suite of natural rocks. Figure 53 illustrates results on metamorphosed granites and gneisses from western Greenland plotted on an isochron diagram of $^{87}Sr/^{86}Sr$ against
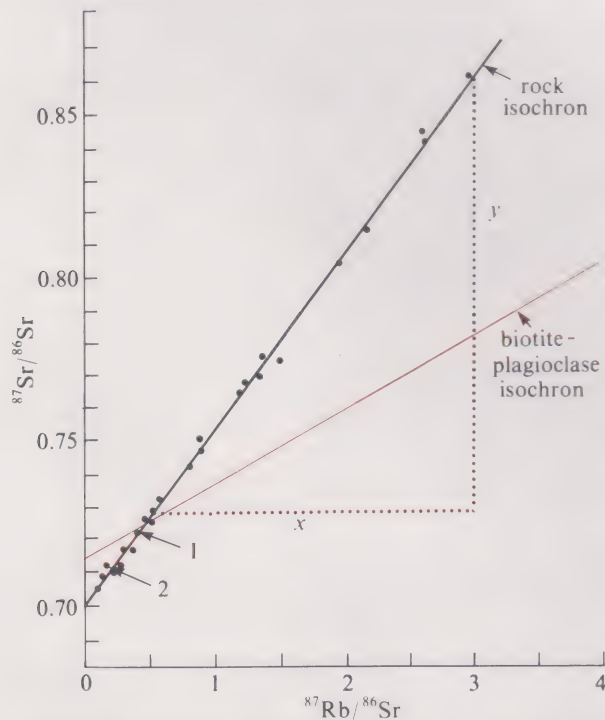

FIGURE 53 An isochron diagram presenting analyses of metamorphosed granites and gneisses from western Greenland. The slope of the isochron = y/x (see text for discussion).

$^{87}Rb/^{86}Sr$. They all fall on or close to a straight line whose slope may be calculated as follows:

The slope of the isochron on Figure 53 is given by y/x. The values of y and x may be read off their respective axes, $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$.

Therefore
$$y = 0.859 - 0.727 = 0.132$$

$$x = 3.0 - 0.5 = 2.5$$

and   the slope $\dfrac{y}{x} = \dfrac{0.132}{2.5} = 0.0528$

From the equations derived earlier, the slope of an isochron $= \lambda t$, where λ (the decay constant) for the decay of $^{87}Rb = 1.42 \times 10^{-11}$ year^{-1}, and represents the fixed probability that 1.42×10^{-11} atoms of ^{87}Rb will decay in a single year.

Therefore, the slope $0.0528 = 1.42 \times 10^{-11} \times t$

$$\text{or } t = \frac{0.0528}{1.42} \times 10^{11}$$

$$= 3.7 \times 10^9 \text{ years}$$

Given that all the assumptions stated above are valid, then these rocks in western Greenland were formed about 3700 million years ago. In fact, they are the oldest rocks known to be preserved on Earth.

From Figure 53, can you determine the initial Sr-isotope ratio $(^{87}Sr/^{86}Sr)_o$ of these western Greenland rocks?

The answer is the value of $^{87}Sr/^{86}Sr$ where that axis is intersected by the isochron, that is, 0.70.

ITQ 30   The red line in Figure 53 is an isochron drawn through the isotope results for biotite mica and plagioclase feldspar which were separated from one of the metamorphosed granites from western Greenland and then analysed. Assume that the slope of this isochron corresponds to the age of those minerals.

(a)   Are these minerals older, younger, or of the same age as the rocks whose age we have just calculated to be 3700 Ma? (You should try to answer this part of the question without doing any calculation—simply compare the slopes of the two isochrons on Figure 53.)

(b)   Calculate the slope and hence the age of the isochron for biotite and plagioclase feldspar ($\lambda = 1.42 \times 10^{-11}$ year^{-1}).

The answer to ITQ 30 illustrates a further point of which you should be aware: *minerals need not be of the same age as their host rock*. In the simplest case, an igneous rock crystallizes and clearly those minerals are of the same age as the rock itself. However, if at some later date the igneous rock is reheated and metamorphosed then new metamorphic minerals will grow. Their age will be that of the metamorphism and will be younger than that of the host rock. The results from western Greenland indicate that while granites and gneisses were formed 3700 Ma ago, they were then reheated so that metamorphic minerals were formed at about 1600 Ma. Moreover, by analysing both the rocks and minerals from different groups of rocks in this area it has been possible to document a fairly complex sequence of geological events.

This topic of how rocks can preserve the isotopic record of the time of their formation, even though the minerals within them are sometimes much younger, is discussed in much more detail in the audio-vision sequence AV 06. This is the ideal point for you to complete AV 06: 'Geochronology: the dating of rocks and minerals', which goes over the equations used to calculate ages using the Rb–Sr decay scheme, and then discusses what may be learnt by dating both separated minerals and their host rocks. The AV sequence will take you about 60 minutes to complete and it starts in the AV Notes, to which you should now refer.

8.3   Initial Sr-isotope ratios

Section 8.2 concentrated on how to determine the age of a rock or a mineral. However, much useful information is also preserved in their initial Sr-isotope ratios. Why is it that different rock types often have different $(^{87}Sr/^{86}Sr)_o$? Why do such ratios tend to be higher in younger rocks? *The short answer is that the value of an initial Sr-isotope ratio reflects both the chemistry (as mirrored in its Rb/Sr ratio) and age of the source region from which the particular rock was derived.* Initial isotope ratios therefore provide a fascinating window through which we may look back at the pre-formation history of many rocks.

In addition, if we determine the initial ratios of rocks of different ages which were derived from the same segment of the Earth (perhaps in the upper mantle, or within continental crust), we should be able to describe its evolution in terms of its changing isotope ratios.

Let us return to our equation for determining the age of a sample from the decay of ^{87}Rb to ^{87}Sr (equation 15),

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right) = \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)\lambda t + \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{o}}$$

We have established that this is in the form of $y = mx + c$, so if we plot a diagram of ^{87}Sr/^{86}Sr against ^{87}Rb/^{86}Sr we should get a straight line with a slope equal to λt (as in Figures 52 and 53). However, we can turn it around and plot another useful diagram in which the slope of a straight line will no longer be λt, but rather $\lambda(^{87}$Rb/^{86}Sr).

Can you see what we need to plot?

A graph of ^{87}Sr/^{86}Sr (y) against time t (x) will also yield a straight line ($y = mx + c$), but in this case the slope (m) is $\lambda(^{87}$Rb/^{86}Sr) while the intercept (c) on the ^{87}Sr/^{86}Sr axis is still (^{87}Sr/^{86}Sr)$_{\text{o}}$. Figure 54 is just such a diagram and its great advantage is that it enables us to illustrate how ^{87}Sr/^{86}Sr ratios *change* with time. It is therefore called an *isotope evolution diagram*.
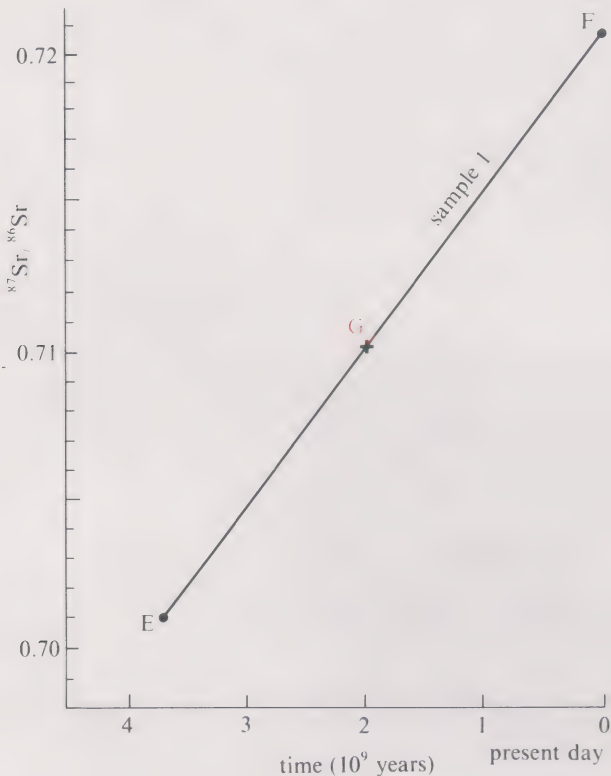
FIGURE 54   An Sr-isotope evolution diagram illustrating the change in the ^{87}Sr/^{86}Sr ratio of sample 1 (Figure 53) from 3 700 Ma (E) to the present day (F).

Consider sample 1 from western Greenland (Figure 53). Its present-day ^{87}Sr/^{86}Sr ratio was measured as 0.720 6 and its initial Sr-isotope ratio (that is, 3 700 Ma ago) was found to be 0.701 from the isochron intercept on Figure 53. We may plot these two ^{87}Sr/^{86}Sr ratios on the isotope evolution diagram (Figure 54) at 0 Ma (point F) and 3 700 Ma (point E) respectively. They are joined by a straight line EF whose slope is $\lambda(^{87}$Rb/^{86}Sr). Moreover, since ^{87}Rb/^{86}Sr is approximately proportional to Rb/Sr (for most rocks ^{87}Rb/^{86}Sr $\approx 2.9 \times$ Rb/Sr), *the slope is also approximately proportional to Rb/Sr*—that is, the higher the Rb/Sr ratio the steeper the slope.

Equally important, however, is the fact that the line EF is the *path* along which this sample evolved from 3 700 Ma to the present day. Thus, if we wish to roll back the clock say 2 000 Ma, we may use the line EF to read off what the Sr-isotope ratio of this sample was at that time. 2 000 Ma ago it was at point G and its ^{87}Sr/^{86}Sr ratio was therefore 0.710.

(Note also that although we stated that (^{87}Sr/^{86}Sr)$_{\text{o}}$ is the intercept on the ^{87}Sr/^{86}Sr axis on diagrams such as Figure 54, we have not actually continued the line EF to intersect the ^{87}Sr/^{86}Sr axis. Two points are relevant: (i) The sample did not exist before 3 700 Ma ago and thus we cannot justify continuing the line back beyond E.

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(ii) Strictly, we should therefore draw the $^{87}Sr/^{86}Sr$ axis at the age of the sample (in this case through the point E). However, that would mean drawing different axes for samples of different ages and would make it difficult to compare such samples. Thus for clarity we draw just one Sr-isotope axis and simply start our straight line at the time of formation of the rock (E in Figure 54).)

> **ITQ 31** A second sample (number 2 in Figure 53) of the 3 700 Ma old granites and gneisses from western Greenland has a present day $^{87}Sr/^{86}Sr$ ratio of 0.709. Plot it on Figure 54 and draw the evolution path of this sample from 3 700 Ma to the present day. What was its Sr-isotope ratio 2 000 Ma ago?

These calculations are all very well, but why should we be bothering to find out about the Sr-isotope ratios of rocks at different times since they were formed? If the history of the rocks since their formation has been uneventful, then indeed there is little point in such calculations. But suppose, for example, that there had been powerful earth movements and re-heating of the western Greenland rocks 2 000 Ma ago, resulting in partial melting and the generation of granitic magmas.

> What would be the $^{87}Sr/^{86}Sr$ ratio of a granitic liquid produced by partial melting of sample 1 that occurred 2 000 Ma ago?

Assuming that equilibrium was maintained and the Sr-isotope ratio of the melt was therefore the same as that of the source rock, then a melt of sample 1 formed 2 000 Ma ago would have an $^{87}Sr/^{86}Sr$ ratio of 0.710 (G in Figure 54). Its initial Sr-isotope ratio would be 0.710. Moreover, since you have also shown that, at that time, the $^{87}Sr/^{86}Sr$ ratio of sample 2 was different (0.704 6, ITQ 31) we may distinguish (on the basis of their initial Sr-isotope ratios) between granites derived by remelting sample 1 or 2. These and similar arguments can be applied to resolve quite complicated geological problems, and we shall look at one later in this Section. First, however, we need to consider the important topic of the evolution of the Earth's mantle, the ultimate source of most igneous rocks, to find out what strontium isotopes have to tell us about that.

8.4 $^{87}Sr/^{86}Sr$ ratios in oceanic volcanic rocks and their bearing on models for mantle evolution

In Section 7.4 we used incompatible trace-element ratios to argue that many basalts erupted on ocean islands and along ocean ridges could not have been derived by partial melting of source material with the same trace-element geochemistry. Thus there must be variations in at least the trace-element chemistry of the upper mantle rocks beneath the ocean basins. Moreover, as illustrated by ITQ 28, these include variations in Rb/Sr and so, from what we now know about the decay of ^{87}Rb to ^{87}Sr (Section 8.2), we may predict that *with time* differences in $^{87}Sr/^{86}Sr$ will also develop.

Figure 55 summarizes some of the Sr-isotope results reported from young (less than 50 Ma old) volcanic rocks erupted in oceanic areas. Because they were formed
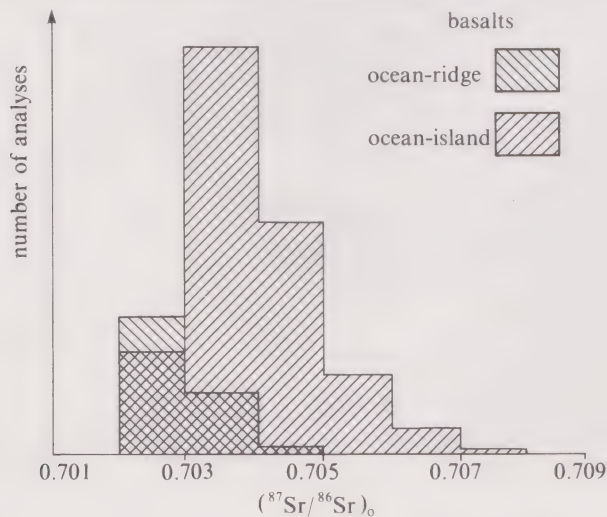

FIGURE 55   Histogram of $(^{87}Sr/^{86}Sr)_o$ ratios (i.e. *initial* Sr-isotope ratios) reported from selected suites of recent oceanic volcanic rocks.

comparatively recently, their measured present-day $^{87}Sr/^{86}Sr$ ratios are very similar to their initial Sr-isotope ratios. Clearly, significant variations in $^{87}Sr/^{86}Sr$ do occur in the upper mantle source regions of these volcanic rocks, and it is noticeable that those from ocean-ridge basalts tend to be lower than those from ocean-island basalts. Moreover, this is consistent with the answer to ITQ 28, which indicated that the source regions for ocean-ridge basalts also have *lower* Rb/Sr ratios than the sources of ocean-island basalts.

Let us now put these results into perspective relative to the evolution of the planet Earth as a whole. The Earth is about 4 550 Ma old (as you learned from Block 1, Section 2) and it has many chemical similarities with *chondrites*[A]. Thus, since the Earth formed at the same time and from the same materials as chondrite meteorites, it is generally believed to have had the same initial Sr-isotope ratio, 0.699. For reasons to be discussed in Block 7, the Earth is also believed to have an overall Rb/Sr ratio of about 0.03, and we may therefore use these data to plot the evolution of the average or bulk Earth on an Sr-isotope evolution diagram—line AB in Figure 56.
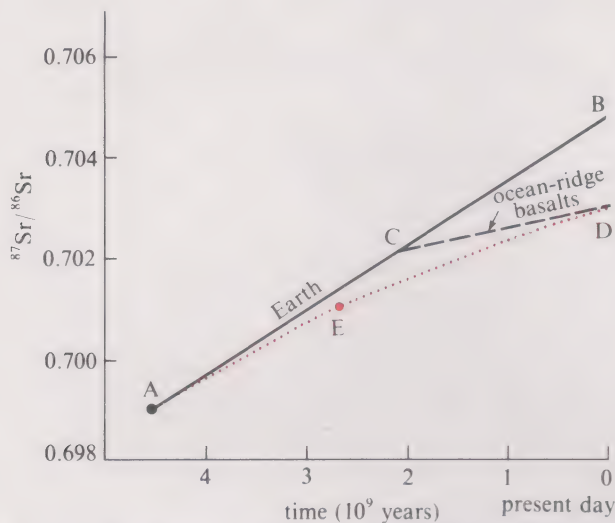
FIGURE 56   Sr-isotope evolution diagram comparing possible evolution paths for the source regions of ocean-ridge basalts. B is calculated using equation 15, taking the average Rb/Sr ratio of the Earth to be 0.03, its age to be 4.55 Ga, and its initial $^{87}Sr/^{86}Sr$ ratio (point A) to be 0.699 (see text). Remember that the slope of a line on a Sr-isotope evolution diagram depends on the Rb/Sr ratio of the particular sample or system. (C. D and E are explained in the text.) 'Ocean-ridge basalts' means 'the upper-mantle source of ocean-ridge basalts'.

In addition to representing the evolution of the whole Earth, the line AB depicts the evolution of any segment of the Earth in which the Rb/Sr ratio has remained unchanged for the last 4 550 Ma. (Strictly speaking, of course, Rb/Sr decreases with time as ^{87}Rb decays to ^{87}Sr (ITQ 29), but since that causes the Rb/Sr ratio of the Earth to change by less than 1/10 of 1 per cent, we may ignore it in this discussion.) It is significant therefore that the overwhelming majority of mantle-derived rocks from the ocean basins have $^{87}Sr/^{86}Sr$ ratios that are *different* from the present-day calculated value for the Earth (about 0.705, see Figure 56). Hence we must conclude that the Rb/Sr ratios in the source regions of these volcanic rocks are also different from that of the Earth as a whole, and that they have therefore been changed (by processes other than that of radioactive decay) during the evolution of the Earth.

> In general, the $^{87}Sr/^{86}Sr$ ratios of the oceanic volcanic rocks tend to be *lower* than that of the bulk Earth (compare the results in Figure 55 with the position of B in Figure 56). Does that suggest that their upper mantle source areas have higher or lower Rb/Sr ratios than the bulk Earth?

Lower, since *lower* Rb/Sr ratios will with time result in *lower* $^{87}Sr/^{86}Sr$ ratios.

> Think back to the Section on the partial melting of peridotite. Did the Rb/Sr ratio of a partial melt tend to be slightly higher or lower than that in the original source rock?

Rb tends to be more incompatible than Sr during the melting of peridotite (Figure 49), and thus particularly small volumes of partial melt tend to have slightly higher Rb/Sr ratios than their original source rocks.

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How then might upper mantle rocks come to have *lower* Rb/Sr ratios than the bulk Earth?

The simplest way of reducing the Rb/Sr ratio of a piece of mantle is to remove a small amount of (partial) melt from it. Moreover, since the Earth's crust is made up of material ultimately derived by partial melting in the mantle, *many isotope geologists now believe that the low $^{87}Sr/^{86}Sr$ ratios of these upper mantle rocks reflect the extraction of partial melts to form the Earth's crust.*

Some consequences of this idea will be further developed later in this Course: it bears on whether large-scale convection occurs in the whole mantle, or just the upper parts of it (which will be discussed in Block 4), and it is the cornerstone on which many models for the chemical evolution of the Earth are presently balanced (which will be discussed in Block 7). In the rest of this Section we shall confine ourselves to one particular question, namely:

The overwhelming majority of recent volcanic rocks erupted in the ocean basins are formed along ocean ridges and these have surprisingly uniform $^{87}Sr/^{86}Sr$ ratios with an average of 0.703 (Figure 55). Providing that their source rocks have the same Sr-isotope ratios, most of the upper mantle from which recent igneous rocks are derived would also appear to have an average $^{87}Sr/^{86}Sr$ ratio of 0.703, and as argued earlier, this indicates that it must also have had comparatively *low* Rb/Sr ratios. Can we deduce how long these segments of the upper mantle have had low Rb/Sr ratios?

Ocean-ridge basalts have an average Rb/Sr ratio of about 0.01 and, since they reflect more than 10 per cent partial melting of peridotite, we may assume that their upper-mantle source rocks have similar Rb/Sr ratios (Section 7.4). We may therefore use the Rb/Sr ratio of 0.01 with equation 15 to calculate their $^{87}Sr/^{86}Sr$ ratios at earlier times and so plot the evolution of these segments of upper mantle on the Sr-isotope evolution diagram (Figure 56). Their evolution path projects back in time until it intersects the Earth evolution path at about 2 100 Ma ago (point C in Figure 56).

Given that two important assumptions are upheld:

(i) that our models for partial melting are reasonably correct and so the Rb/Sr ratios of the ocean-floor basalts are the same as in their source rocks, and

(ii) that the Rb/Sr ratios in the source rock have remained unchanged for 2 100 Ma,

then the simplest interpretation is to envisage that the upper mantle had the same Rb/Sr ratio as the Earth from 4 550 to 2 100 Ma ago. Its composition therefore evolved along the line AC in Figure 56. At point C (2 100 Ma ago), some catastrophic event took place within the mantle which depleted the source of ocean-ridge basalt in Rb relative to Sr, and since then its $^{87}Sr/^{86}Sr$ ratio has evolved along the line CD.

Such a model for mantle evolution is called a *two-stage* model (AC and CD in Figure 56). Its main disadvantage is that we have no idea why or how a catastrophic event took place 2 100 Ma ago. Also there is a second and slightly more subtle objection concerning the relationship between the sources of ocean-ridge and ocean-island basalts. We have seen that they have different $^{87}Sr/^{86}Sr$ and Rb/Sr ratios (Figure 55 and discussion) indicating that variations in at least isotopes and trace elements occur in the upper mantle, probably due to the migration of particularly small volumes of partial melt throughout its evolution. The two-stage model, as outlined above, stipulates that the Rb/Sr ratio in the source region of ocean-ridge basalts has remained unchanged—it cannot, for example, have interacted with the source regions of ocean-island basalts—for 2 100 Ma. The second objection to the two-stage model is therefore that it is difficult to believe that in a continually mobile, convecting, upper mantle, the source regions of these two types of basalts could have managed to have remained separate and isolated for such a very long period of time.

two-stage isotopic evolution model

If the Rb/Sr ratio in the source of ocean-ridge basalts changes continuously with time, how would it plot on Figure 56?

Evolution with a roughly constant Rb/Sr ratio plots as a straight line on Figure 56 and thus, if the Rb/Sr ratio changes continuously, the slope changes continuously and it must plot as a curve. In the case of the source of ocean-ridge basalts we believe it starts at A with the Rb/Sr ratio of the Earth (0.03) and finishes at D with the Rb/Sr ratio of ocean-ridge basalts (0.01). The slope thus becomes flatter with time and the curved evolution path might be similar to AD in Figure 56. Such a model is called a *continuous evolution* model.

continuous isotopic evolution model

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In practice, these *two-stage* and *continuous evolution* models are likely to be over-simplifications—they are end-member concepts between which a whole series of multi-stage models may be envisaged. Also, they do not take into account what happens if convection causes mixing in the upper mantle. Their basic difference is that the two-stage model implies that before 2 100 Ma ago the mantle source regions of magmatic rocks all had the same Rb/Sr ratio, and that that was the same as that for the Earth (0.03). In contrast, the continuous evolution hypothesis suggests that chemical variations (as reflected in different Rb/Sr ratios) were present in the upper mantle from very early in Earth history.

How might we test these two extreme models?

The easiest way is to determine the initial $^{87}Sr/^{86}Sr$ ratio of a rock derived from the upper mantle before 2 100 Ma. The two-stage model predicts that it should plot *on* the line AC (Figure 56), while the continuous model predicts that it should plot *below* the line AC, possibly on the curve AD.

Studies of areas of very old rocks in Canada, Greenland, Southern Africa and Australia have revealed that there was considerable magmatic activity in all these areas about 2 700 Ma ago. The initial $^{87}Sr/^{86}Sr$ ratio in many of the mantle-derived rocks is 0.701, and this plots below the Earth evolution line on Figure 56 (point E). Thus we may conclude that, in sharp contradiction to the predictions of the two-stage model, those portions of the upper mantle sampled by magmatism had already been depleted in Rb relative to Sr by 2 700 Ma.

Such a conclusion supports the view that throughout the history of the Earth the crust has been extracted by magmatic, or igneous, processes from at least the upper mantle. The crust will have slightly higher, and the residual mantle slightly lower, Rb/Sr ratios than the original mantle. At the present time crust is formed by melting beneath mid-ocean ridges and along subduction zones (Section 4.1, Block 1). But has it always happened that way? Moreover, has the rate of formation of the crust always been the same? In Block 7 we shall consider some of the geological evidence that the style of global tectonic processes may have been different early in earth history, and some thermal arguments to suggest that the *rate of formation* of the crust has slowed down through time. In Block 4 we shall look at the nature of convection, and in particular enquire whether the whole mantle, or just the upper part, has contributed material to the formation of the Earth's crust.

8.5 Initial Sr-isotope ratios and the genesis of granites

In Section 6 we concluded that intermediate and acid magmas could be derived both from the mantle (via fractional crystallization of more basic magmas) and by partial melting of crustal rocks. The first mechanism represents the formation of *new* continental crust, whereas in the second pre-existing crustal material is simply being remelted and redistributed. Since both may result in granitic end-products with the same major-element composition, the latter cannot be used to establish the origin of such rocks—we must turn instead to their isotope geochemistry and in particular to their initial Sr-isotope ratios. We shall illustrate this point by considering a suite of granites from Namibia that have recently been the subject of detailed geochemical work.

Namibia is a large, but thinly populated country in south-west Africa. It contains a belt of granitic rocks bearing unusually high concentrations of uranium. The uranium deposits occur in and along the margins of granites, which were formed during a mountain-building event some 650–450 Ma ago, and it is because the source rocks of the granites may well have been the source of the uranium that they have been the subject of so much research interest.

Available knowledge about the geology of Namibia suggests that the granites could be derived from:

(i)   the upper mantle; or

(ii)   2 000 Ma old granites and gneisses; or

(iii)   younger, but still pre-650 Ma, sediments that now lie on those older gneisses.

Let us consider the evolution of $^{87}Sr/^{86}Sr$ in each of these three possible source materials. The upper mantle was discussed in Section 8.4, where it was emphasized that the upper mantle source regions for ocean-ridge basalts have low $^{87}Sr/^{86}Sr$ ratios, whereas those for ocean-island basalts tend to have slightly higher

$^{87}Sr/^{86}Sr$ ratios—closer to that of the average bulk Earth (Figures 55 and 56). In continental areas, the upper mantle has Sr-isotope ratios similar to those beneath ocean islands and, for the sake of this discussion, we have therefore assumed that the upper mantle beneath Namibia has the same Rb/Sr and $^{87}Sr/^{86}Sr$ ratios as the bulk Earth (it evolves along the line AB in Figure 57).
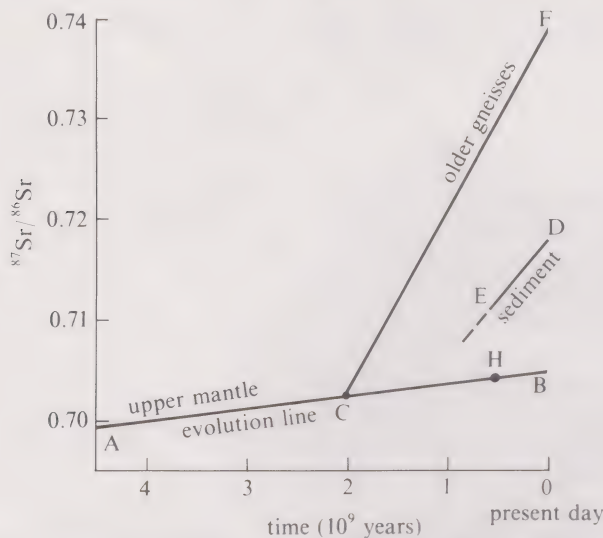

FIGURE 57 Sr-isotope evolution diagram illustrating the different evolution paths for the possible source materials for the Namibian granites (see text for discussion).

Typical samples of the older gneisses have present day $^{87}Sr/^{86}Sr$ ratios of 0.74, they are 2 000 Ma old and their initial Sr-isotope ratios are 0.702. Since at that time at least parts of the upper mantle had the same $^{87}Sr/^{86}Sr$ ratios (point C in Figure 57), it is argued that these old granites and gneisses were derived from the upper mantle—they are thought to represent the formation of new continental crust from the mantle 2 000 Ma ago. Note that their Rb/Sr ratios are significantly higher than those in the mantle rocks and that they therefore evolve along a line of steeper slope on a Sr-isotope evolution diagram such as Figure 57.

> From our discussions of how Rb/Sr ratios in the liquid change during partial melting and fractional crystallization processes, why should these typical crustal rocks have higher Rb/Sr ratios than their mantle source rocks?

Rocks with higher SiO_2 content are either produced by small degrees of partial melting, or a lot of fractional crystallization from more basic magmas of minerals including plagioclase feldspar, and in either case the Rb/Sr ratio of the resultant granitic liquid will be higher than that in the original source rocks (see Sections 6 and 7).

Less is known about the younger sediments, and in particular we do not know exactly how old they are—nonetheless, this need not affect our argument. Representative samples of these sediments have an average present-day $^{87}Sr/^{86}Sr$ of 0.718 (point D, Figure 57). They therefore evolved along the line DE, although because we do not know their exact age we do not know where the line should be started.

In summary, the trends in Figure 57 represent the best available estimate of how the Sr-isotope ratios of the three likely source regions for the granites have evolved with time. If $^{87}Sr/^{86}Sr$ and Rb/Sr are determined for several samples of each granite, then their age and initial Sr-isotope ratio may be calculated using the isochron diagrams (Figures 52 and 53). We shall consider results from just two granites—one that contains high concentrations of uranium and one that does not.

> The uranium-poor granite gave an age of 550 Ma and an initial Sr-isotope ratio of 0.704 5. Where does that plot in Figure 57?

It plots at point H, which is on the mantle evolution line (AB) and we would therefore conclude that this uranium-poor granite appears to have been derived from the upper mantle.

> ITQ 32 The uranium-rich granite by contrast is both younger (480 Ma) and has a higher initial Sr ratio (0.730). Plot these results on Figure 57. What is the most likely source material for this granite?

Thus, Sr-isotopes have enabled us to argue that the granites that contain high concentrations of uranium were derived from a different source region from those that do not. Moreover, by sampling likely source rocks and assessing how their Sr-isotope ratios changed with time (Figure 57) we have been able to conclude that the uranium-rich granites were probably derived by remelting 2 000 Ma old granites and gneisses. As stated earlier in Section 8, initial Sr-isotope ratios (of the granites, in this case) depend on both the chemistry (as reflected in the Rb/Sr ratio) and the age of the source rocks.

8.6 Summary of Section 8

(a) Some isotopes are unstable and they decay, emitting radiation—this is the process of *radioactive decay*. It is described by the law of radioactive decay, which states that the rate at which the numbers of radioactive atoms decrease is proportional to the numbers of atoms which are present. The rate of disintegration is exponential, yet the rate of decay (as expressed by the decay constant λ) is *constant* for any particular isotope species.

(b) Isotope decay schemes, such as $^{87}Rb \longrightarrow {}^{87}Sr$, may be used to determine the ages of both rocks and minerals. For Rb and Sr ages were calculated using an isochron diagram ($^{87}Sr/^{86}Sr$ against $^{87}Rb/^{86}Sr$) on which samples of the same age and initial Sr-isotope ratio plot on a straight line whose slope is approximately equal to λt.

(c) Initial Sr-isotope ratios, $(^{87}Sr/^{86}Sr)_o$, are those present when a sample is formed. They reflect both the age and the chemistry (as mirrored in different Rb/Sr ratios) of the source rock(s) from which the sample in question was derived. Consequently, they are widely used to assess the nature of the source particularly of igneous rocks—for example, whether granitic rocks are derived from the upper mantle or the crust.

(d) By determining the initial Sr-isotope ratios in rocks of different ages we may also map out how a particular source region, such as the upper mantle, has evolved with time. This in turn, provides important constraints on models of how the Earth as a whole has evolved.

8.7 Objectives for Section 8

Now that you have completed Section 8, you should be able to:

1 Define in your own words, and recognize formal definitions of, the terms flagged in the margins of this Section.

30 Describe the decay of ^{87}Rb to ^{87}Sr and understand what happens to the different isotope ratios of Rb and Sr with the passage of time.

31 Plot $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ results on an isochron diagram and determine both the age of the samples and their initial Sr-isotope ratio.

32 Explain in your own words the assumptions that must be upheld if a suite of samples are to plot on a single isochron so that their true age may be calculated from its slope (λt).

33 Use initial Sr-isotope ratios to evaluate the likely source of particular igneous rocks.

34 Use Sr-isotope evolution diagrams to illustrate how $^{87}Sr/^{86}Sr$ ratios in different rocks change with time.

Apart from Objective 1, to which they all relate, the four ITQs in this Section test these Objectives as follows: ITQ 29: Objective 30; ITQ 30: Objective 31; ITQ 31: Objective 33; ITQ 32: Objective 34.

You should now do the following SAQs, which test other aspects of these Objectives.

SAQ 25 (*Objective 31*)   Plot the results for the six rocks in Table 10 in Figure 58. Draw a straight line through at least five points; calculate the slope of the isochron and hence the age of the samples. (λ for $^{87}Rb = 1.42 \times 10^{-11}$ year^{-1}.)

SAQ 26 (*Objective 32*)   Think back to the assumptions that must be upheld if the correct age is to be determined using an isochron diagram. Can you suggest *two* reasons why one of the samples in Table 10 does not fall on the isochron with the other five samples?

TABLE 10   Data for SAQs 25–27

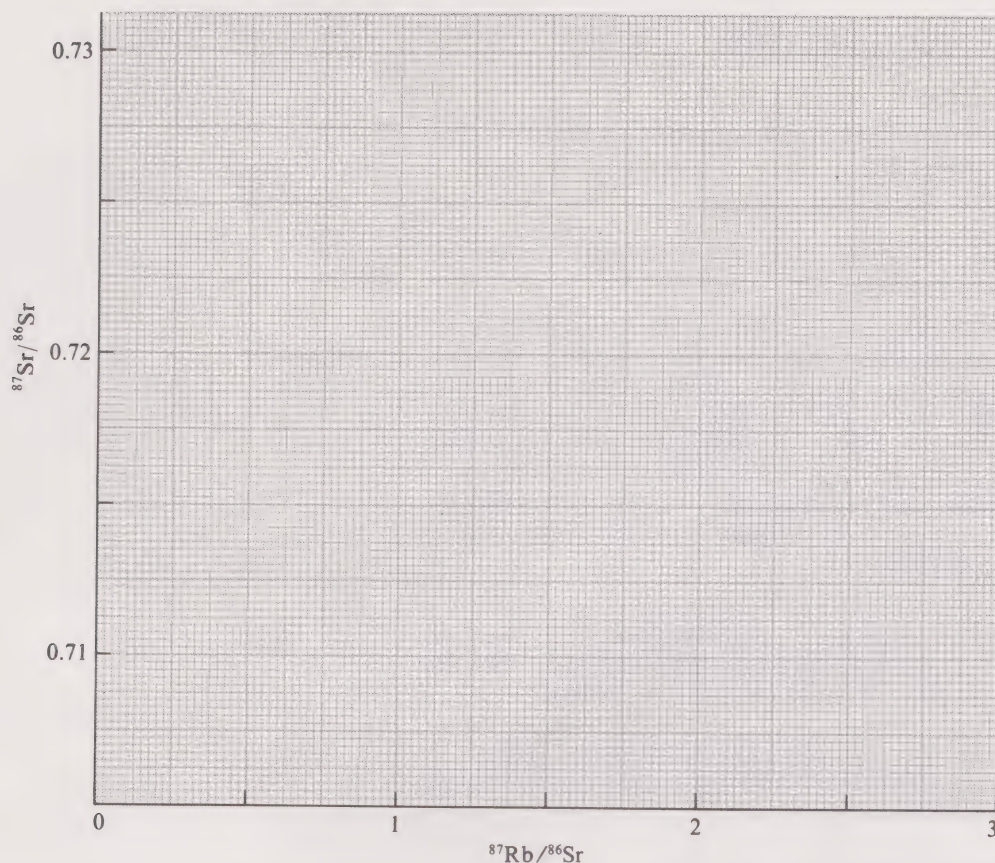| Sample	$^{87}Sr/^{86}Sr$	$^{87}Rb/^{86}Sr$
1	0.713 0	0.12
2	0.718 7	0.95
3	0.724 5	1.75
4	0.726 2	2.00
5	0.725 0	2.50
6	0.731 0	2.70

FIGURE 58   Graph of $^{87}Sr/^{86}Sr$ against $^{87}Rb/^{86}Sr$, for use with SAQ 25.

SAQ 27 (*Objective 33*)   What is the initial Sr-isotope ratio of the five samples on the isochron in Figure 58? If they were samples of another granite from Namibia, would their initial Sr-isotope ratio indicate that they were derived from (a) the upper mantle, (b) younger sediments, or (c) the older gneisses in Figure 57?

Optional further reading

Brownlow, A. H. (1979) *Geochemistry*. Prentice-Hall, Englewood Cliffs, N.J.

Cox, K. G., Bell, J. D. and Pankhurst, R. J. (1979) *The Interpretation of Igneous Rocks*. George Allen and Unwin, London.

Faul, H. (1966) *Ages of Rocks, Planets and Stars*. McGraw-Hill, New York.

Faure, G. (1977) *Principles of Isotope Geology*. John Wiley & Sons, New York.

Acknowledgements

Appendix 1 The phase rule

(i) Introduction

The phase rule relates the numbers of phases and components in a system which are present at equilibrium. It states that:

$$P + F = C + 2$$

where P = number of *phases* co-existing, F = number of *degrees of freedom* and C = minimum number of *components*.

Phase was defined in the text (Section 2.1), but both degrees of freedom and component warrant careful consideration. A *component* is simply a part of a whole—however, what we call a component in turn depends on our frame of reference. Take the example of a motor car. The engine is a major component of the car, and yet within it there are smaller parts (carburettor, plugs, and so on), which in practice are referred to as components, or parts, of the engine. The use of the term component depends on whether our frame of reference is the car itself, or simply the engine. As we shall see later, similar choices await us in describing components in both chemical and geological systems.

<div style="float:right">**component, C**</div>

The second point to notice about the term C in the phase rule is that it is the *minimum* number of components. Formally, *it is the minimum number of components both necessary and sufficient to describe the composition of all phases within the particular system.* That, if you like, lays down our frame of reference.

> How many components can you recognize in the H_2O system (Figure 5, p. 11)? What is the minimum number of components necessary to describe the *composition* of all the phases in that system?

All the phases (ice, water, and water vapour) have the same composition. They may therefore be described by the *one* component H_2O, and the system in Figure 5 is consequently a *one-component system*.

> But H_2O consists of both hydrogen and oxygen. Why is it not therefore a two-component system?

The answer lies in the definition of C in the phase rule—it is the *minimum* number of components necessary to describe the composition of all the phases in the system, that is, one is better than two!

The term F, *degrees of freedom*, can be defined as the minimum number of variables that must be fixed in order to define perfectly a particular condition of the system; that is, a particular location on a phase diagram. Usually the temperature and/or pressure must be stated. However, the composition and/or the number of phases may also be fixed.

<div style="float:right">**degrees of freedom, F**</div>

If, in the H_2O system, we stipulate that the conditions are such as to allow the three phases (ice, water, and water vapour) to exist together, the phase diagram (Figure 5b) shows that there is only one point, T, at which this is possible. The coexistence of these three phases is possible only at *one* particular pressure and temperature, and those may be read off the axes of the diagram. It is not necessary to state values of pressure and temperature to define the condition of the system—we have been able to do that by simply stipulating that the three phases co-exist. Using the phase rule, we have stated that $P = 3$, and since H_2O is a one-component system, $C = 1$; therefore

$$P + F = C + 2$$
$$3 + F = 1 + 2$$

Therefore,
$$F = 0$$

Three phases co-existing in a one-component system lead to a condition where $F = 0$. The number of degrees of freedom is zero (nothing can change without something else changing) and this is called a condition of *invariance*. The point T in Figure 5b (the triple point) is an *invariant point*. Neither pressure or temperature may vary (no freedom) without causing one or two of the phases to be eliminated.

<div style="float:right">**invariant point**</div>

> Where on a phase diagram, such as that for H_2O, do *two* phases co-exist?

The two phases co-exist on the *phase boundaries* (see Section 2.1).

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ITQ 33 Use the phase rule to calculate how many degrees of freedom exist on a phase boundary ($P = 2$) in a one-component system.

Consider the phase boundary between ice and water (curve B) in Figure 5b. The answer to ITQ 33 indicated that on such a phase boundary there was one degree of freedom. To stipulate that ice and water co-exist does not uniquely define the conditions of the assemblage (since they may co-exist anywhere along curve B); we must also stipulate *either* the temperature or the pressure. For example, if ice and water co-exist at $-5\,°C$ the pressure must be about 0.001 kbar, since they lie on curve B. Such phase boundaries, on which there is one degree of freedom, are called *univariant*. All the curves on Figure 5b are *univariant curves*.

univariant curve

The third situation to consider in the H_2O system is *within* the stability fields of ice, water, or water vapour. In this case only one phase is present and, using the phase rule, we may again calculate the number of degrees of freedom.

$$P + F = C + 2$$
$$1 + F = 1 + 2$$

Therefore,
$$F = 2$$

When one phase is present in a one-component system, there are two degrees of freedom—the stability fields of ice, water and water vapour in Figure 5b are *divariant* regions. Since the individual phases are stable under a wide variety of pressures and temperatures it is necessary to stipulate *both* in order to define the conditions of the system.

divariant

In summary, you should note first that systems may be classified in terms of the number of components: H_2O is a one-component system. Second, from the phase rule and the number of phases present, the degrees of freedom of any combination of phases *that co-exist in equilibrium* may be calculated. A *divariant* assemblage may be subject to change in *two* variables—pressure and temperature (or composition in systems with more than one component). A *univariant* assemblage (as on the phase boundaries in Figure 5b) only has *one* degree of freedom; thus it will only be maintained if a change in one variable is accompanied by a specific (dependent) change in the other. Our example was to move *along* the phase boundary between ice and water. An *invariant* assemblage of phases (the triple point T, Figure 5b) can be maintained only if the variables are not allowed to change—it has *no* degrees of freedom.

(ii) At a eutectic point

The significance of a eutectic point in a two-component system, as illustrated in Figure 12, p. 19, may be simply demonstrated using the phase rule. If we stipulate that three phases co-exist (crystals of G, crystals of H, and the liquid) then since it is a two-component system (G and H), we can calculate the number of degrees of freedom:

$$P + F = C + 2$$
$$3 + F = 2 + 2$$

Therefore,
$$F = 1$$

At a eutectic point in a two-component system there is one degree of freedom. Thus if we fix either the pressure, the temperature, or the composition, then neither of the other two variables can change without reducing the number of phases which can co-exist in equilibrium. However, we have stated that diagrams such as Figure 12b depict phase relations *at constant pressure*. Thus for any particular diagram of temperature against composition the pressure is fixed, and we must conclude that there is only one point (the eutectic) where the three phases can co-exist in equilibrium.

(iii) Melting a sample of 80 per cent An, 20 per cent Di

On heating the sample of 80 per cent An and 20 per cent Di (Figure 13), the first liquid appeared (at the eutectic point) when the temperature reached $1\,275\,°C$. As more heat is added, the crystals and the liquid remain at that temperature until all the crystals of Di have melted.

In Section (ii) of this Appendix it was demonstrated that at a eutectic point in a two-component system, there is only one degree of freedom. Now once the crystals of Di have melted and only two phases are left in the system (crystals of An, and the

liquid), then from the phase rule we may deduce that there must be an extra degree of freedom. Two phases are co-existing in a two-component system, therefore:

$$P + F = C + 2$$
$$2 + F = 2 + 2$$

Therefore,
$$F = 2$$

At the eutectic point, where three phases were in equilibrium, there was only one degree of freedom: now, above the eutectic, there are only two phases, $F = 2$, that is, there are two degrees of freedom. Remember, however, that the phase diagram in Figure 13 is at constant pressure, and thus, if we fix either the temperature or the composition, we will have stipulated the two degrees of freedom. Put another way, the liquid will remain on the liquidus so long as two phases are present, thus, if we stipulate the temperature, we may read off the composition of the liquid. For example, at $1\,400\,°C$ the liquid (which is at L_3, Figure 13) is 58 per cent An, 42 per cent Di.

Once the temperature is above $1\,500\,°C$, our sample moves into the liquid-only field. Attempt ITQ 34, to check that you understand how the number of degrees of freedom has changed.

> **ITQ 34** Use the phase rule to calculate the number of degrees of freedom for a sample in the liquid-only field in the Di–An system. Can you name those degrees of freedom?

Objectives for this Block

When you have completed this Block, you should be able to:

1 Define in your own words, or recognize valid definitions of, the terms, concepts and principles listed in Table A (in some way all the ITQs and SAQs in this Block are related to this Objective).

2 Explain why the composition of a liquid produced by partial melting differs from that of the original rock. (ITQ 1; SAQ 2)

3 Indicate that you understand the difference between crystallization and fractional crystallization, and why the latter tends to change the composition of the bulk sample. (ITQ 2)

4 Use diagrams of pressure against temperature and temperature against time to describe what happens to selected samples under different conditions of temperature and pressure. (ITQs 3 and 4; SAQ 3)

5 Undertake simple calculations using the phase rule; e.g. calculate the number of degrees of freedom that exist for a particular assemblage of phases (Appendix 1). (ITQ 33; SAQ 4)

6 Recognize and be able to explain the significance of the main features of a two-component eutectic phase diagram. (ITQs 5 and 8; SAQ 5)

7 Use a phase diagram to describe the crystallization and melting behaviour of a sample made up of a mixture of two components between which there is no solid solution. (ITQs 5, 6 and 8; SAQ 6)

8 Discuss conditions at different locations on such phase diagrams in terms of the phase rule (Appendix 1). (ITQ 34)

9 Interpret textures in suitable igneous rocks in terms of crystallization paths on a eutectic phase diagram. (ITQ 7; SAQ 7)

10 Recognize and explain the significance of the main features on a phase diagram of temperature against composition for a binary system within which there is solid solution between the two end-members. (SAQ 8)

11 Use such phase diagrams to describe crystallization and melting behaviour of samples made up of mixtures of two components between which there is solid solution. (ITQ 9; SAQ 8)

12   For two-component systems, calculate how much crystallization has taken place when a sample is at a particular temperature—that is, for particular compositions of the crystals and the liquid. (ITQ 10; SAQ 9)

13   Explain in your own words the effects of non-equilibrium crystallization in simple two-component eutectic and solid-solution systems. (ITQ 11; SAQ 10)

14   Plot the composition of a sample consisting of a mixture of three components on a triangular variation diagram. (ITQ 12; SAQ 11)

15   Describe the equilibrium crystallization and melting behaviour of a sample in a ternary system. (ITQ 13; SAQ 12)

16   Calculate the composition of a sample from the relative proportions of its minerals and their analyses. (ITQ 14)

17   Use mixing calculations to estimate the amount of fractional crystallization required to change the composition of a liquid by a particular amount. (ITQ 15; SAQ 16)

18   Understand the consequences of non-equilibrium crystallization in a ternary system such as Di–Ab–An. (ITQ 16; SAQ 13)

19   Describe, using chemical variation diagrams, the relationship between crystallizing minerals and the evolution of a liquid. (ITQs 17 and 18, SAQs 15 and 19)

20   Plot the compositions of a suite of igneous rocks (and of their phenocryst minerals) on a variation diagram and assess whether the individual rocks could be related to one another by fractional crystallization. (ITQ 18; SAQs 14 and 15)

21   Describe equilibrium and non-equilibrium crystallization and melting in the binary system Or–Ab. (ITQ 20; SAQ 18)

22   Discuss partial melting and crystallization in the synthetic granite system Qz–Ab–Or. (ITQ 21; SAQ 19)

23   Outline briefly two ways in which intermediate and acid (granitic) magmas may be formed. (SAQ 20)

24   Calculate partition coefficients and use them to predict qualitatively how a particular trace element is distributed between co-existing crystals and liquid. (ITQ 23; SAQ 21)

25   Calculate what happens to the concentrations of trace elements in a magma during fractional crystallization of different minerals. (ITQs 22 and 24; SAQ 21)

26   Explain in your own words the factors that control whether a trace element will be able to substitute readily into a particular mineral.

27   Calculate *bulk* partition coefficients for a rock containing two or more minerals. (ITQ 26; SAQ 22)

28   Use a simple model for partial melting to calculate the distribution of different trace elements at different degrees of partial melting. (ITQs 25 and 26; SAQs 23 and 24)

29   Use the ratios of incompatible trace elements in igneous rocks to estimate those in their primary magmas, and hence in their original source rocks. (ITQs 27 and 28; SAQs 22, 23 and 24)

30   Describe the decay of ^{87}Rb to ^{87}Sr and understand what happens to the different isotope ratios of Rb and Sr with the passage of time. (ITQ 29)

31   Plot $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ results on an isochron diagram and determine both the age of the samples and their initial Sr-isotope ratio. (ITQ 30; SAQ 25)

32   Explain in your own words the assumptions that must be upheld if a suite of samples are to plot on a single isochron so that their true age may be calculated from its slope (λt). (SAQ 26)

33   Use initial Sr-isotope ratios to evaluate the likely source of particular igneous rocks. (ITQ 31; SAQ 27)

34   Use Sr-isotope evolution diagrams to illustrate how $^{87}Sr/^{86}Sr$ ratios in different rocks change with time. (ITQ 32)

ITQ answers and comments

ITQ 1 In the basalt, Al_2O_3, CaO and FeO are more abundant and MgO is much less abundant, than in the peridotite. The abundance of the fifth constituent, SiO_2, is very similar in both rocks.

ITQ 2 (a) The olivine and peridotite have similar compositions (note particularly that in each case SiO_2 and MgO together make up over 85 per cent of the total) and this suggests that peridotite must contain a lot of olivine.

(b) We have argued that basalt consists predominantly of the lower-temperature minerals in peridotite, because basalt is produced by partially melting peridotite. Since the composition of the olivine and the basalt are significantly different, it suggests that the basalt does not contain a lot of olivine. That in turn suggests that olivine is not a low-, but rather a relatively high-temperature mineral.

ITQ 3 The answers are illustrated in Figure 59.

(a) The temperature does not change (that is, the graph is horizontal) while a phase change is taking place. The lower-temperature phase change ($0\,°C$) is ice to liquid water, while the higher-temperature phase change ($100\,°C$) is water to vapour (steam).

(b) H_2O exists as ice below $0\,°C$, as liquid water between $0\,°C$ and $100\,°C$, and as steam (or hot water vapour) above $100\,°C$.

(c) H_2O was present as *just* liquid water from 14 to 34 minutes, that is, for 20 minutes.

(d) Liquid water co-exists with ice and steam respectively while the two phase changes are taking place at $0\,°C$ and $100\,°C$. Thus some liquid water was present from 8 to 42 minutes, i.e. 34 minutes.

ITQ 4 In Figure 5b, the slope of the freezing (or melting) point curve is negative; and, as ice is less dense than water (ice cubes float!), ΔV for the reaction liquid water $\longrightarrow$ ice is positive. Thus, because the slope is negative, ΔV and ΔH must have opposite signs, and so ΔH is negative. The reaction liquid water $\longrightarrow$ ice is *exothermic*.

ITQ 5 The answers refer to Figure 11b.

(a) The first crystals appear at the temperature T_4.

(b) The composition of the crystals must be either 100 per cent G or 100 per cent H, since we have stated that there is no solid solution between them. In this case the sample is rich in H and the first crystals to form are 100 per cent H (answer (ii)) and these have been plotted at temperature T_4 on the right-hand axis of Figure 11b.

(c) The correct answer is again (ii). As crystals of H are forming, the liquid must become richer in G.

(d) Temperature T_6. Yes, it is the same temperature as observed for sample 1.

(e) The percentages of G and H in the completely solid sample are the same as in the original liquid, 90 per cent H and 10 per cent G.

ITQ 6 The answers are illustrated in Figure 60.
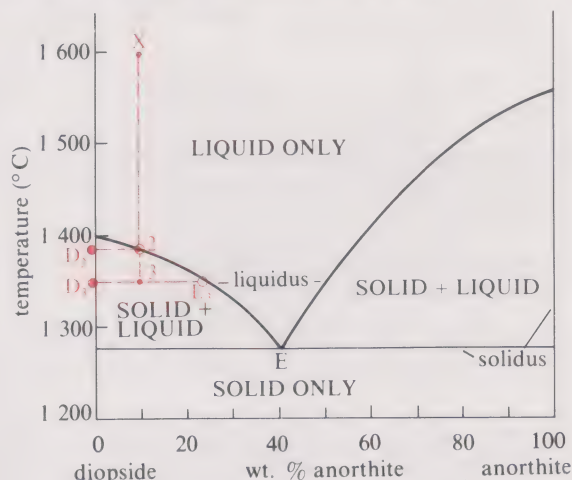

FIGURE 60 Answer to ITQ 6.

(a) The first crystals appear in the sample consisting of 10 per cent An and 90 per cent Di when it plots on the liquidus, that is, at $1\,380\,°C$, point 2 (Figure 60). The crystals plot on the solidus at the same temperature (D_2, Figure 60) and consist of 100 per cent Di (0 per cent An).

(b) Liquids co-existing with crystals plot on the liquidus. For samples such as this one, which are rich in Di, the liquid has a composition of 25 per cent An (and thus 75 per cent Di) at a temperature of $1\,350\,°C$, that is, at L_3 in Figure 60. The tie-line linking the total sample, and the crystals and liquid that co-exist at that time is the line D_3–3–L_3.

(c) Yes, tie-lines will be horizontal on phase diagrams of temperature against composition because crystals and liquid that co-exist *in equilibrium* will be *at the same temperature*.

(d) Crystals of Di and An can only crystallize together at the eutectic point (E), which in Figure 60 is at $1\,275\,°C$.

(e) The composition of the final solid is the same as that of the original liquid, 10 per cent An, 90 per cent Di.
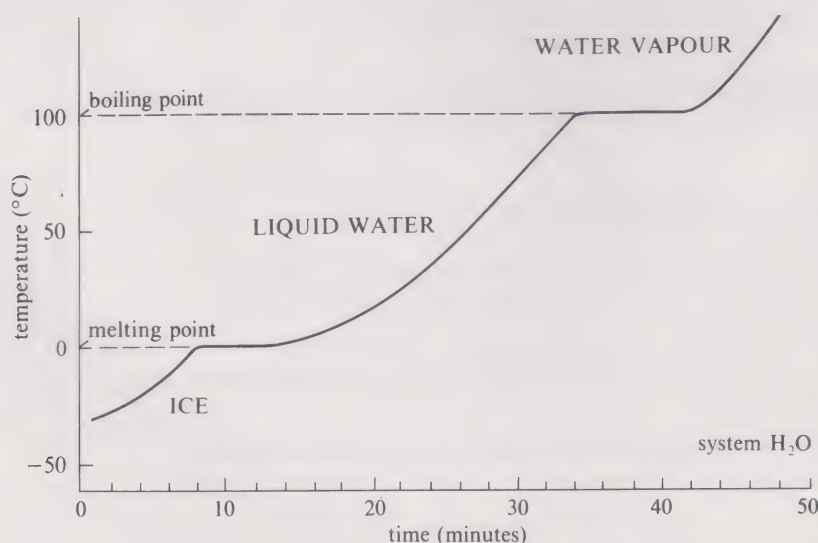

FIGURE 59 Answer to ITQ 3.

ITQ 7 (a) The same argument applies to the second photo-micrograph in Figure 14 as it did to the first; see the text. In the second case, however, the phenocrysts are of diopside, which suggests that, while those crystals were forming, the sample was in the left-hand solid-and-liquid field on the Di–An phase diagram (Figure 13). Thus the rock must contain relatively more diopside than the eutectic mixture of 60 per cent diopside, 40 per cent anorthite, and for a sample in the left-hand solid-and-liquid field the temperature was between 1 275 and 1 400 °C (Figure 13).

(b) The only place on the phase diagram (Figure 13) where diopside and anorthite crystallize *together* is at the eutectic point E. Figure 14c might therefore represent a eutectic liquid (composition 60 per cent diopside, 40 per cent anorthite) that crystallized at 1 275 °C.

ITQ 8 (a) The lowest temperature at which liquid can still be present is at the eutectic point E, that is, at −21 °C. The composition of the liquid at E is 29 per cent NaCl, 71 per cent H_2O.

(b) The first crystals appear at about 4 °C, the temperature on the liquidus curve at the composition of 40 per cent NaCl. However, because this sample is on the NaCl-rich side of the eutectic composition (at E) the crystals are of pure NaCl! The addition of this much salt to ice on roads at −10 °C still leaves the mixture in the solid-and-liquid field. Thus solid NaCl co-exists with a liquid consisting of a mixture of H_2O and NaCl and, since no ice is present, we may conclude that the ice did all melt, but that we used much more NaCl than was necessary!

(c) At −10 °C, ice will be in equilibrium with salt water containing 18–20 per cent NaCl (that is, the total sample will be in the left-hand solid-and-liquid field) until there is about 20 per cent NaCl—whereupon the ratio of H_2O:NaCl is about 80:20 or 4:1. For every 100 g of ice, therefore, about 25 g of salt must be added. Since this will give a mixture in which the ice and salt water are exactly in equilibrium, slightly more salt than this would need to be added to induce melting.

ITQ 9 The answers refer to Figure 61.

(a) A sample of An_{70} contains 70 per cent anorthite and 30 per cent albite, so the answer is 30 per cent albite.

(b) The first crystals appear when the total sample first plots on the liquidus. For a sample of An_{70} this occurs at a temperature of 1 490 °C.

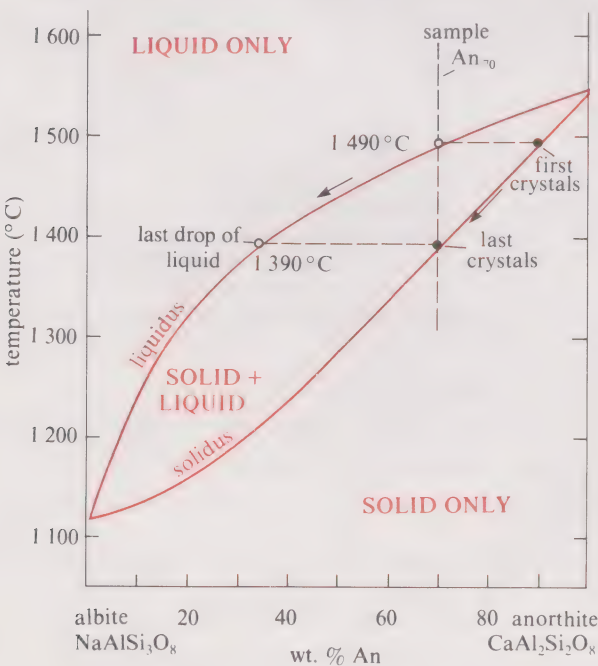(c) The first crystals plot on the *solidus* at that same temperature of 1 490 °C; their composition is therefore An_{89}.

FIGURE 61   Answer to ITQ 9.

(d) The composition of the *total* sample does not change, therefore it is still An_{70}.

(e) The sample becomes completely solid when the total sample moves from the solid-and-liquid to the solid-only field, that is, when it crosses the solidus. For a sample of An_{70}, this occurs at a temperature of 1 390 °C.

(f) The last drop of liquid before crystallization is complete plots on the liquidus at that temperature of 1 390 °C. The composition of the liquid at 1 390 °C is An_{33}.

(g) The composition of the crystals in equilibrium with the last drop of liquid is very close to that of the total sample, that is, An_{70}.

ITQ 10 The answer is illustrated in Figure 62. At 1 435 °C, the sample of An_{50} plots in the solid-and-liquid field at point s, the liquid is at point l, and the crystals are at point c (Figure 62).

From Figure 17 and the text,

$$\text{percentage of crystals at c} = \frac{sl}{cl} \times 100$$

From Figure 62, $sl = 1$ mm and $cl = 20$ mm. Therefore

$$\text{percentage of crystals at c (1 435 °C)} = \frac{1}{20} \times 100$$
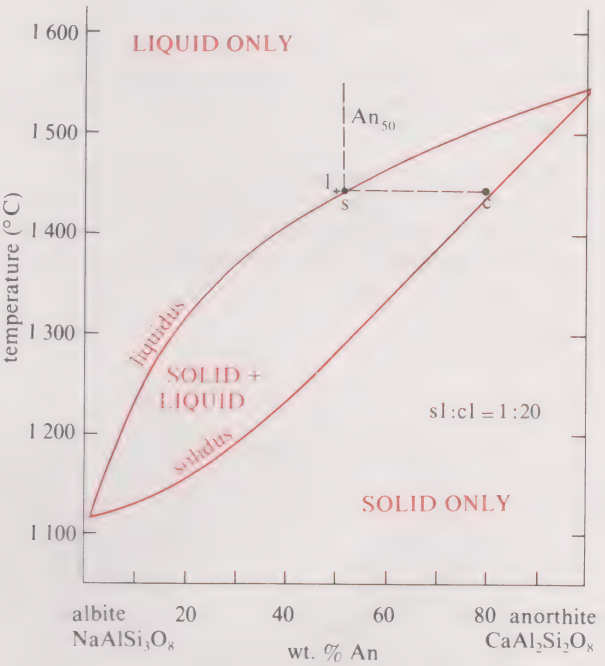
$$= 5 \text{ per cent}$$

FIGURE 62   Answer to ITQ 10.

ITQ 11 The answers are illustrated in Figure 63.

(a) On cooling, a sample of Fo_{60} first intersects the liquidus at point a and thus the first crystals plot on the solidus at the same temperature (point b). Their composition is Fo_{86}. The sample Fo_{60} leaves the solid-and-liquid field at point e and under equilibrium conditions the composition of the last crystals is the same as the total sample, that is, Fo_{60}.

(b) Crystals of Fo_{83} plot on the solidus at point c—at a temperature of 1 700 °C. The co-existing liquid is on the liquidus (point d) at the same temperature (1 700 °C), and its composition is Fo_{54}.

(c) If after 20 per cent crystallization the crystals (Fo_{83}) and the liquid (Fo_{54}) become isolated from each other, then we may consider their crystallization separately. If the continuing crystallization of the liquid is under equilibrium conditions, then the composition of the final crystals is the same as that of that liquid (Fo_{54}). Thus, when solidification of the *total* sample Fo_{60} is complete, there are crystals of Fo_{83} and Fo_{54}. The sample consists of 20 per cent of the former
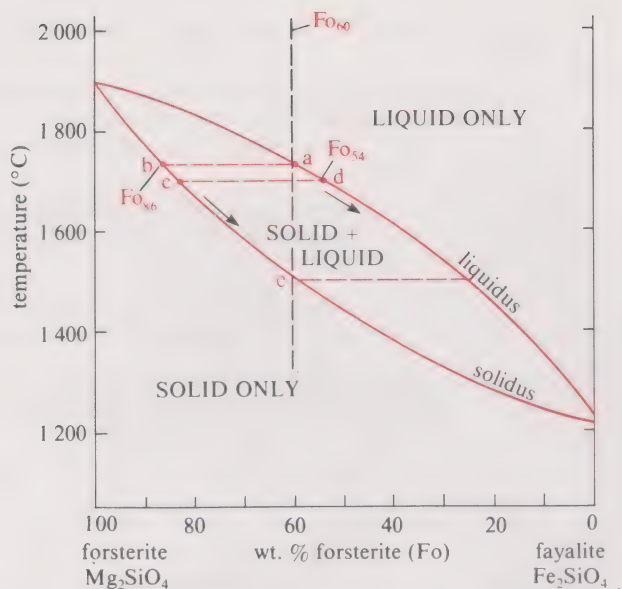
95

FIGURE 63   Answer to ITQ 11.

and 80 per cent of the latter because those were the percentages of the crystals and liquid when they were isolated at 1 700 °C. See also Figure 19 and the discussion of the plagioclase system.

(d)   Forsterite is Mg-rich and fayalite is Fe-rich: thus, since the early crystals are relatively rich in *forsterite* they have *higher* Mg/Fe ratios than those that form at lower temperatures which are richer in *fayalite*.

ITQ 12   The two samples are plotted on a triangular diagram in Figure 64. Sample (i) consists of 14 per cent Di (Q), 43 per cent Ab (R) and 43 per cent An (P), and since these proportions are already expressed as percentages they may be plotted directly (see Figure 64).
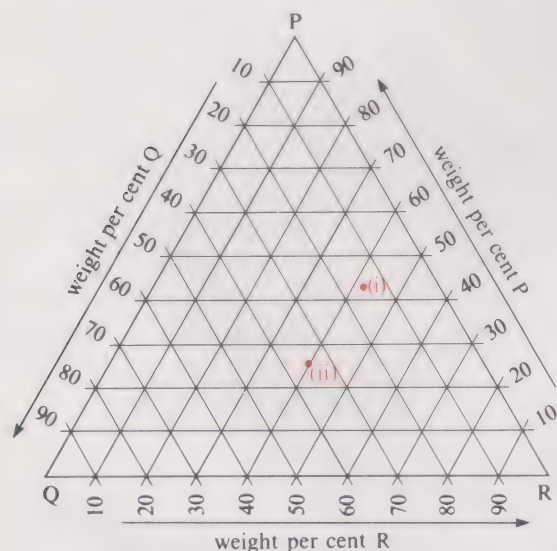
FIGURE 64   Answer to ITQ 12.

Sample (ii) contains 70 g diopside (Q) + 80 g albite (R) + 50 g anorthite (P) and the total is therefore 200 g.

When we re-calculate the amounts of anorthite, albite and diopside as percentages, we get:

$$\text{diopside (Q)} = \frac{70 \times 100}{200} = 35 \text{ per cent}$$

$$\text{albite (R)} = \frac{80 \times 100}{200} = 40 \text{ per cent}$$

$$\text{anorthite (P)} = \frac{50 \times 100}{200} = 25 \text{ per cent}$$

These percentages may then be plotted directly onto Figure 64. Note that you only actually need to calculate the percentages of two of the minerals to plot the sample on such a diagram. But it is useful to calculate the third, as a check on your answer.

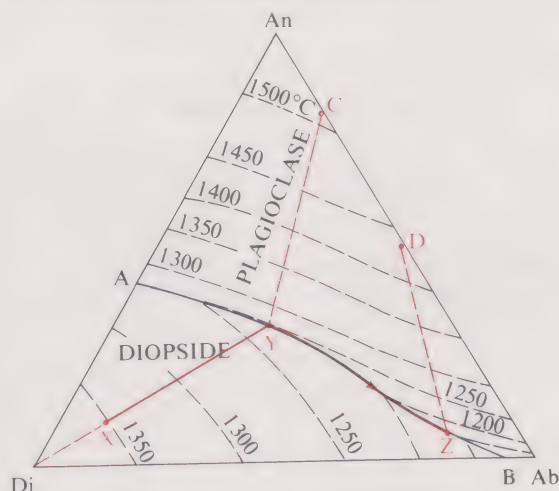**ITQ 13**   The answers are illustrated in Figure 65.

FIGURE 65   Answer to ITQ 13.

(a)   A composition of 80 per cent Di, 10 per cent Ab, and 10 per cent An plots at point X in Figure 65. The liquidus surface is at 1 350 °C at this composition and hence that is the temperature at which the first crystals start to form.

(b)   Because point X plots on the diopside-rich side of the cotectic curve (AB, Figure 65), diopside crystallizes first. With further cooling, the composition of the remaining melt moves directly away from the diopside apex of the triangle and intersects the cotectic curve at about 1 235 °C (point Y). At this temperature, plagioclase starts to crystallize with diopside. These two minerals crystallize together as the melt cools along the cotectic curve, until crystallization is complete (point Z). Naturally, the plagioclase composition changes as crystallization proceeds.

(c)   The first plagioclase to crystallize at 1 235 °C (point Y) from this melt has the composition C (An_{80}), as in the text example we described. This is because the Ab:An ratio is the same in both melts; that is, 1:1, so effectively the composition of plagioclase in the liquid is An_{50}. At this stage the liquid and the plagioclase crystals effectively plot on the liquidus and solidus respectively for compositions on the cotectic curve projected onto the Ab–An face of Figure 24. The composition of the plagioclase changes from C to D (Figure 65) as the sample cools and, since the crystals at D have the same composition (An_{50}) as the plagioclase in the original liquid, then under equilibrium conditions they must be the last crystals of plagioclase to form. The composition of the bulk sample X plots on the straight line between the crystals at D and the Di apex (Figure 65). Finally, the last drop of liquid has the composition of Z simply because that is the point on the cotectic curve (AB) where the temperature is the same as that of those last plagioclase crystals at D, that is, 1 160 °C. The composition of Z in Figure 65 is the same as that of M in Figures 24 and 25, precisely because the composition of the plagioclase in the original sample is the same in each case. (*Note*   You were not asked to deduce the composition of the last drop of liquid.)

ITQ 14 Al_2O_3 in liquid =

$(Al_2O_3$ in diopside$) + (Al_2O_3$ in albite$) + (Al_2O_3$ in anorthite$)$

but, for example, Al_2O_3 in diopside =

(wt. % Al_2O_3 in diopside) × (proportion of diopside in the liquid).

So Al_2O_3 in liquid $= \left(0 \times \dfrac{14}{100}\right) + \left(19.4 \times \dfrac{43}{100}\right) + \left(36.6 \times \dfrac{43}{100}\right)$

$$= 0 + 8.34 + 15.7$$

$$\approx 24.0 \text{ per cent}$$

Similarly, for Na_2O,

$$Na_2O \text{ in liquid} = \left(0 \times \frac{14}{100}\right) + \left(11.8 \times \frac{43}{100}\right) + \left(0 \times \frac{43}{100}\right)$$

$$= 0 + 5.07 + 0$$

$$\approx 5.1 \text{ per cent.}$$

ITQ 15 (a) From Figure 30,

$$AB = 24 \text{ mm, } AL = 38 \text{ mm and } BL = 14 \text{ mm}$$

The quantity of crystals of A which must be crystallized for the composition of the liquid to evolve from B to L is given by:

$$\text{weight per cent of A} = \frac{100 \, BL}{AL}$$

Therefore,

$$\text{weight per cent of A} = \frac{100 \times 14}{38} = 37$$

(b) AB now $= 10 \text{ mm}$, therefore $AL = 24 \text{ mm}$ and

$$\text{weight per cent of A} = \frac{100 \times 14}{24} = 58$$

Thus, although the change in the composition of the liquid is the same in each case, much more crystallization is required when the composition of the crystals is closer to that of the liquid (answer to (b)).

ITQ 16 (a) In a simple binary eutectic system such as Di–An (Figure 13), the compositions of the minerals are fixed. Thus, whether or not they are in equilibrium with the liquid, their composition cannot change and the composition of the liquid at any particular temperature will therefore be the same whether crystallization takes place under equilibrium or non-equilibrium conditions.

(b) (ii). As illustrated in Figure 19, residual liquids produced by non-equilibrium crystallization in the plagioclase system will be richer in albite than those produced under equilibrium conditions.

ITQ 17 (i) The cumulate C is the one sample that represents crystals—it consists only of olivine.

(ii) The composition of samples A, B and D are most likely to represent liquids. A and D are fine-grained and thus cooled rapidly. B contains phenocrysts of olivine but it does not appear to have lost or gained crystals on cooling and thus its composition is also likely to be similar to that of a liquid.

ITQ 18 The answer is illustrated in Figure 66. The CaO (14.2 per cent) and SiO_2 (44.5 per cent) contents of the aggregate phenocryst assemblage plot on-line with the trend of the lavas with 52–58 per cent SiO_2. Removal of an extract of that composition would therefore drive the composition of the residual liquid along the trend of those lavas. We may conclude that fractional crystallization of that phenocryst assemblage could be responsible for the variations in CaO and SiO_2 in the lavas with 52–58 per cent SiO_2.

ITQ 19 The answer is also illustrated in Figure 66, where the extract 14.2 per cent CaO, 44.5 per cent SiO_2 is labelled A, the liquid at 50 per cent SiO_2 is B and the liquid at 66 per cent SiO_2 is C. From Figure 66, $AB = 21 \text{ mm, } BC = 58 \text{ mm}$ and therefore $AC = 79 \text{ mm}$.

(a) From the mixing calculation (Section 5.2),

$$\text{weight per cent of A} = \frac{100 \, BC}{AC}$$

$$= \frac{100 \times 58}{79}$$

$$= 73 \text{ per cent}$$

Therefore 73 per cent of the sample must be removed as crystals (the extract) to change the composition of the liquid from 50 to 66 per cent SiO_2.

(b) If the SiO_2 content of the extract assemblage increases, it moves closer to the composition of the liquid. In ITQ 15 we calculated that to change the composition of a liquid by a certain amount required much more fractional crystallization if the composition of the crystals is close to that of the liquid. We may conclude that if the extract becomes richer in SiO_2 our answer to (a) is too low—in practice, *more than* 73 per cent crystallization will be required to change the composition of the liquid from 50 to 66 per cent SiO_2.

ITQ 20 The answers are illustrated in Figure 67 (overleaf).

(a) Melt A has a composition Or_{15}. When this cools to intersect the liquidus, the solid phase that forms is on the solidus at the same temperature and must have the composition Or_7. Melt B has the composition Or_{30} and, when this cools to intersect the liquidus, because the liquidus and solidus coincide, the crystals will have the same composition as the liquid, Or_{30}. Melt C has a composition of Or_{70}. The crystals formed when this melt is cooled to the liquidus have a composition of Or_{88}.

(b) If equilibrium between the crystals and the liquid is maintained throughout crystallization, then the composition of the last crystals to form will be the same as that of the total sample, that is, for $A = Or_{15}$, for $B = Or_{30}$ and for $C = Or_{70}$.
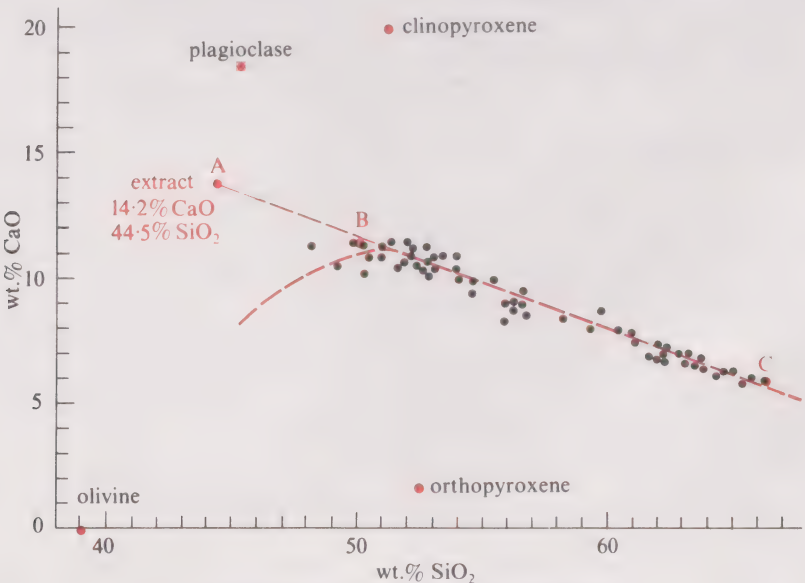
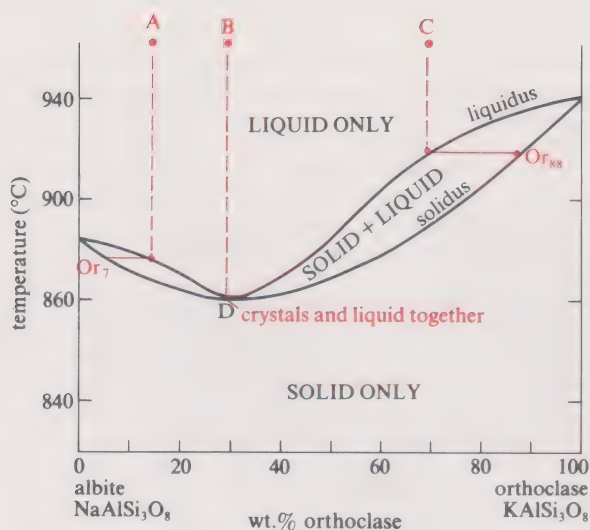

FIGURE 66   Answers to ITQs 18 and 19.

FIGURE 67   Answer to ITQ 20.

ITQ 21   The answer is illustrated in Figure 68.

Upon cooling a liquid with composition R, crystals of pure quartz separate and the melt moves towards the cotectic curve AMB, with further cooling and crystallization of more quartz. The point at which the liquid will reach this curve can be determined by drawing a straight line from the quartz apex, through point R, to the cotectic curve. At this point (S in Figure 68) the melt will begin to crystallize an alkali feldspar, which will be homogeneous, but very rich in the albite component.
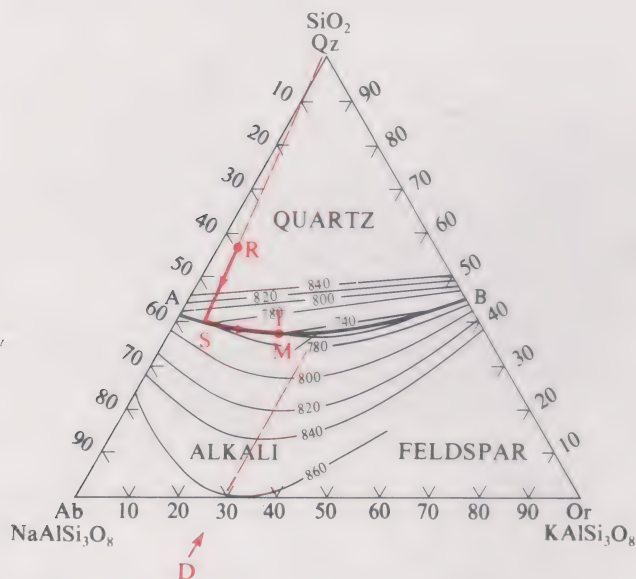
FIGURE 68   Answer to ITQ 21.

As both alkali feldspar and quartz continue to crystallize, the remaining liquid moves down the cotectic curve (towards M). As this occurs, the composition of the alkali feldspar changes by reaction with the melt—both crystals and liquid become richer in orthoclase (see also albite-rich compositions in Figure 39).

(a)   If the equilibrium between crystals and liquid is maintained throughout crystallization, solidification is complete when the crystals of alkali feldspar have the same composition as the feldspars in the original samples (that is, approximately Or_{13}) and at that stage the liquid plots at point T on the cotectic curve AMB (Figure 68).

(b)   If equilibrium is not maintained, the *liquid* moves further down the cotectic curve and may reach the minimum point M. If the crystals and liquid are separated, that is, if fractional crystallization takes place, then the final liquid will form a solid with the same composition as that at the granite minimum (M).

ITQ 22   From the mixing calculation (Section 5.2), the weight per cent of olivine = 100 BA/OA. From Figure 44, BA = 19 mm and OA = 76 mm. Therefore the weight per cent of olivine = 100 × 19/76 = 25.

Thus 25 per cent of olivine crystallization is required to change the composition of the liquid from basalt B to andesite A in Figure 44.

ITQ 23   (a)   The partition coefficient (K_D) for Sr distributed between pyroxene (17.5 p.p.m.) and basalt B (250 p.p.m.) in Figure 44 is given by

$$K_D = \frac{\text{concentration of Sr in pyroxene}}{\text{concentration of Sr in basalt B}}$$

$$= \frac{17.5}{250}$$

$$= 0.07$$

(b)   If the concentration of Sr in the crystallizing mineral is greater than that in the liquid, that is, if the partition coefficient is greater than one (for example, Sr in plagioclase), crystallization *reduces* the concentration of Sr in the liquid. Conversely, if the partition coefficient is less than one (for example, Sr in olivine and pyroxene), the concentration of Sr in the liquid *increases* with increasing crystallization.

ITQ 24   From Figure 45, after 40 per cent fractional crystallization of pyroxene,

$$\frac{C_1}{C_o} \text{ for Rb } (K_D = 0.001) = 1.67$$

Since the concentration of Rb in the original magma (C_o) was 1 p.p.m., then

$$C_1 = 1.67 \times 1 = 1.67 \text{ p.p.m.}$$

Similarly,

$$\frac{C_1}{C_o} \text{ for Sr } (K_D = 0.07) = 1.62$$

but for Sr, $\qquad\qquad C_o = 10 \text{ p.p.m.}$,

therefore, $\qquad\qquad C_1 = 1.62 \times 10$

$$= 16.2 \text{ p.p.m.}$$

After 40 per cent fractional crystallization of pyroxene, the magma contains 1.67 p.p.m. Rb and 16.2 p.p.m. Sr. Its Rb/Sr ratio is 1.67/16.2 = 0.103. Since the Rb/Sr ratio of the original magma was 1/10, or 0.100, the change in Rb/Sr during fractional crystallization was three parts in a hundred, that is 3 per cent. Thus, although the two partition coefficients differ by a factor of *seventy* and the Rb and Sr concentrations have increased by some 60 per cent (that is, 1 to 1.6, Figure 45), the *ratio* of Rb/Sr has changed by *only three per cent*.

ITQ 25   Equation 4 in the text states that

$$C_1 = \frac{C_o}{D + F(1 - D)}$$

For our sample with 65 per cent anorthite and 35 per cent diopside, $C_o = 10$ p.p.m. Rb, and $D = 0.045\,9$ for Rb. Thus, substituting in that equation, we may calculate the concentration of Rb in the liquid (C_1) when $F = 0.25$.

$$C_1 = \frac{10}{0.045\,9 + 0.25\,(1 - 0.045\,9)}$$

$$= \frac{10}{0.045\,9 + 0.239}$$

$$= 35.1$$

After 25 per cent partial melting ($F = 0.25$) the concentration of Rb in the liquid is 35.1 p.p.m.

ITQ 26   (a)   The sample consists of 65 per cent anorthite and 35 per cent diopside. The bulk partition coefficient (D) for Sr is

$$D = (X_o K_D)_\alpha + X_o K_D)_\beta$$

where α = anorthite, β = diopside and X_o and K_D are respectively the initial proportions (expressed between 0 and 1) and partition coefficients for each mineral.

Therefore, $\qquad D = (0.65 \times 2.2) + (0.35 \times 0.07)$

$$= 1.43 + 0.025$$

$$= 1.46$$

(b) The equation for partial melting is:

$$C_1 = \frac{C_o}{D + F(1 - D)}$$

$D = 1.46$ (as calculated above), $C_o = 10$ p.p.m., and thus we may calculate the concentration of Sr in the liquid after 15 per cent partial melting ($F = 0.15$):

$$C_1 = \frac{10}{1.46 + 0.15(1 - 1.46)}$$

$$= \frac{10}{1.46 - 0.069}$$

$$= 7.19$$

After 15 per cent partial melting, the concentration of Sr in the liquid is 7.19 p.p.m.

ITQ 27 (a) For both Rb and Sr, C_1/C_o is always greater than one and at small degrees of partial melting it is very large indeed. Thus both Rb and Sr are strongly concentrated in the liquid.

(b) After 5 per cent partial melting, C_1/C_o is about 20 for Rb and 17 for Sr (Figure 49).

$$C_o \text{ for Rb} = 0.8 \text{ p.p.m.}$$

Therefore, $\qquad C_1 \text{ for Rb} = 20 \times 0.8 = 16 \text{ p.p.m.}$

$$C_o \text{ for Sr} = 25 \text{ p.p.m.}$$

Therefore, $\qquad C_1 \text{ for Sr} = 17 \times 25 = 425 \text{ p.p.m.}$

Thus the concentrations of Rb and Sr in the liquid after 5 per cent partial melting are respectively 16 p.p.m. and 425 p.p.m.

(c) From the inset in Figure 49, the Rb/Sr ratio in the liquid after 10 per cent partial melting (0.035) is 10 per cent higher than that in the original peridotite.

ITQ 28 (a) From the inset in Figure 49, the Rb/Sr ratio in the liquid after 2 per cent partial melting is about 45 per cent higher than that in the original source rock. If the Rb/Sr ratio in the source rock is 0.01, then the Rb/Sr ratio of the 2 per cent melt is $(45/100) \times 0.01 = 0.0045$ higher than that in the source rock; that is, $0.01 + 0.0045 = 0.0145$.

(b) The two basalts in question have Rb/Sr ratios of 0.01 and 0.06—they differ by a factor of 6, or 600 per cent. Your answer to (a) indicates that the maximum variation in Rb/Sr which may be obtained by postulating a 2 per cent partial melt is only 45 per cent. Thus, we must conclude that these ocean-island and ocean-ridge basalts could not have been derived by partial melting of peridotite with the same Rb/Sr ratio.

ITQ 29 (a) ^{87}Rb decays to ^{87}Sr, therefore (i) the ^{87}Rb/^{85}Rb ratio will decrease; (ii) the ^{87}Sr/^{86}Sr ratio will increase, and (iii) the ^{86}Sr/^{84}Sr ratio will not change with the passage of time.

(b) A rock with no Rb cannot generate any ^{87}Sr and thus its ^{87}Sr/^{86}Sr ratio will not change.

(c) Whether Sr is initially present or not, ^{87}Rb will decay and thus the ^{87}Rb/^{85}Rb ratio will decrease.

ITQ 30 (a) The slope of the biotite–plagioclase isochron is *less steep* than that of the rock isochron. The slope equals λt and thus the steeper it is the larger must be the time t. Therefore the minerals must be younger than the rocks.

(b) The slope of the biotite–plagioclase isochron is

$$\frac{0.804 - 0.736}{4 - 1} = 0.02267$$

but the slope $= \lambda t$ and $\lambda = 1.42 \times 10^{-11}$ year^{-1}.

Therefore, $\qquad 0.02267 = \lambda t$

$$t = \frac{0.02267}{1.42 \times 10^{-11}}$$

$$\approx 1600 \text{ Ma}$$

The mineral isochron corresponds to an age of about 1 600 Ma.

ITQ 31 The answer is illustrated in Figure 69. The second sample of the west Greenland granites and gneisses has a present-day ^{87}Sr/^{86}Sr ratio of 0.709. 3 700 Ma ago it had an Sr-isotope ratio of 0.701. It therefore evolved along the line EH on Figure 69. 2 000 Ma ago it was at point I and had an ^{87}Sr/^{86}Sr ratio of 0.704 6.
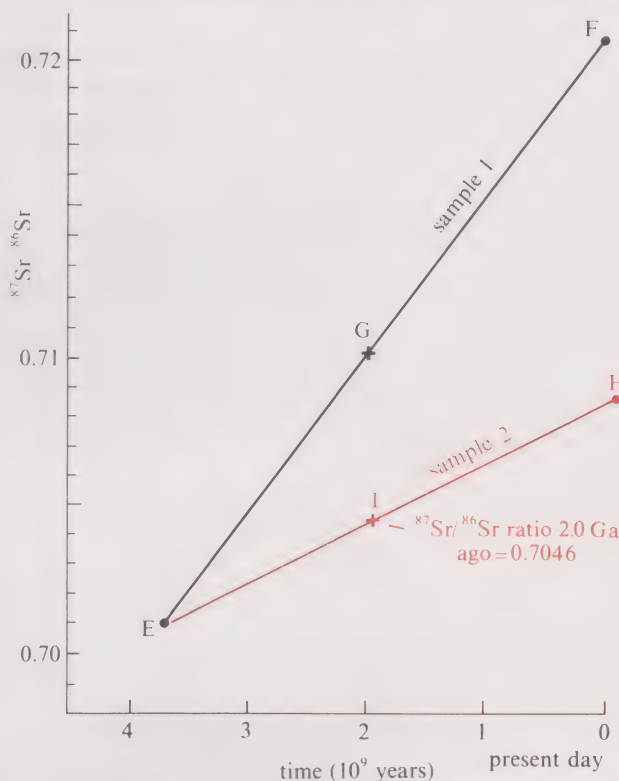

FIGURE 69 Answer to ITQ 31.

ITQ 32 The uranium-bearing granite had an initial Sr-isotope ratio of 0.730, 480 Ma ago. If you plot this point on Figure 57, it falls on the line CF at that time, suggesting that this granite (and thus at least some of the uranium) was derived by remelting of the 2 000 Ma granites and gneisses.

ITQ 33 The phase rule states that:

$$P + F = C + 2 \text{ (see text)}$$

In a one-component system, $C = 1$, and on a phase boundary two phases co-exist and so $P = 2$, therefore:

$$2 + F = 1 + 2$$

$$F = 1$$

We may conclude that on a phase boundary in a one-component system there is one degree of freedom.

ITQ 34 The phase rule states that:

$$P + F = C + 2$$

In a two-component system, such as Di–An, $C = 2$, and in the liquid-only field there is only one phase (the liquid) and so $P = 1$. Therefore,

$$1 + F = 2 + 2$$

$$F = 3$$

In the liquid-only field in a two-component system, there are *three* degrees of freedom: they are *temperature*, *pressure* and *composition*.

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SAQ answers and comments

SAQ 1 (a) Incorrect. *Two* phases co-exist on a phase boundary.

(b) Incorrect. It is only within the liquid-only field that a sample contains no crystals; *on* the liquidus crystals and liquid co-exist.

(c) Correct; see definition of solidus in the text.

(d) Correct; see introduction to Section 1.

(e) Incorrect; latent heat must be *added* to a sample to convert it from solid to liquid.

(f) Correct; see Section 1.

SAQ 2 (i) (a). SiO_2 will be higher in the melt, because olivine has less SiO_2 than the basalt.

(ii) (a). Al_2O_3 will be higher in the melt because olivine contains virtually no Al_2O_3 and thus all the Al_2O_3 is concentrated in the melt.

(iii) (c). Total iron (FeO and Fe_2O_3) will be similar in the melt and the original basalt because the olivine and basalt contain similar amounts of FeO plus Fe_2O_3.

(iv) (b) MgO will be lower in the melt because olivine contains much higher concentrations of MgO than the basalt.

(v) (a). K_2O will be higher in the melt because olivine contains no K_2O.

SAQ 3 The phase boundaries for solid, vapour and liquid in the system carbon are sketched in Figure 70. AT is the melting curve and TB is the boiling curve. There is a triple point at T, at which the pressure is 10^{-1} kbar and the temperature is about 4 300 K.
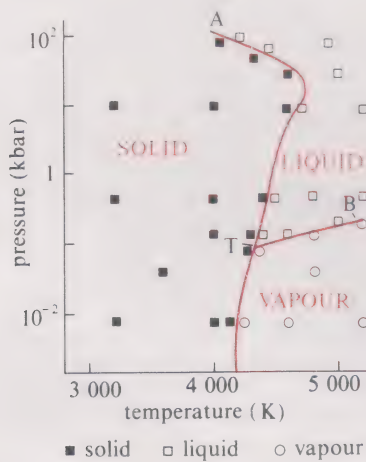

■ solid   □ liquid   ○ vapour

FIGURE 70   Answer to SAQ 3.

SAQ 4 The phase rule states that

$$P + F = C + 2 \text{ (see Appendix 1)}$$

In a one-component system $C = 1$, and if there are four phases $P = 4$; thus

$$4 + F = 1 + 2$$
$$F = -1$$

Since negative values of F indicate that it is impossible for the proposed assemblage of phases to co-exist in equilibrium, we may conclude that four phases cannot co-exist in equilibrium in a one-component system.

SAQ 5 (a) Correct.

(b) Incorrect. In a simple eutectic system, the first crystals to form will have the composition of one of the two components (for example, 100 per cent Di or 100 per cent An in Figure 13).

(c) Correct. See Figures 9, 12 and 13.

(d) Correct, provided that it is a *mixture* that is being heated, not pure end-members.

(e) Incorrect. Between 0 °C and -20 °C in Figure 15 crystals only occur when a sample is in one of the two solid-and-liquid fields, that is, *either* ice *or* salt can occur as crystals, but not both together.

(f) Incorrect. Individual crystals in a simple eutectic system always have the composition of either of the two end-members (for example, 100 per cent Di or 100 per cent An in Figure 13).

(g) Correct.

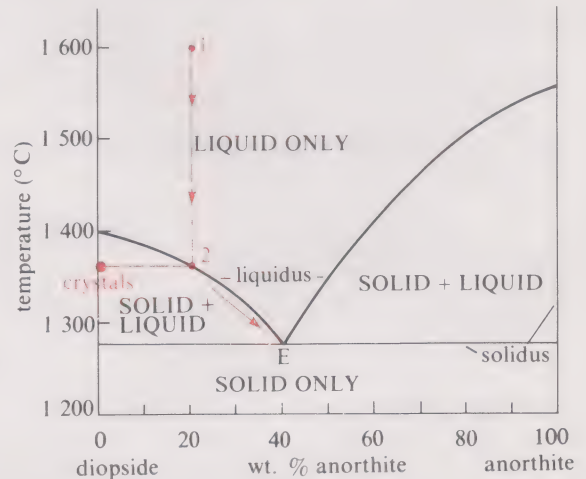**SAQ 6** The answer is illustrated in Figure 71.

FIGURE 71   Answer to SAQ 6.

At 1 600 °C, the sample plots in the liquid-only field (point 1) and it remains there until the temperature falls to 1 360 °C, whereupon it plots on the liquidus (point 2) and the first crystals appear. They are all of the mineral *diopside*. As the temperature falls below 1 360 °C, the total sample moves through the solid-and-liquid field and the crystals plot on the solidus and the liquid moves down along the liquidus. More and more crystals of diopside are formed and thus the liquid becomes richer in anorthite, until at 1 275 °C crystals of anorthite start to appear, crystallizing along with diopside. The temperature remains constant at this point (the eutectic point, E) until the sample is completely solid and it has moved into the solid-only field. Since the last drop of liquid is at the eutectic point E, its composition must be 60 per cent Di and 40 per cent An.

SAQ 7 (i) If the sample of 80 per cent diopside and 20 per cent anorthite were cooled very rapidly from 1 500 °C, it would be very fine-grained (or glassy), since it was completely liquid at that temperature.

(ii) At 1 350 °C, that same sample would be in the solid-and-liquid field and thus it would consist of phenocrysts of diopside set in a fine-grained groundmass (which represents what would still have been liquid at that temperature).

(iii) If this sample cooled slowly to 1 200 °C, it would consist of much coarser crystals of both diopside and anorthite with no fine-grained groundmass since it was already solid.

SAQ 8 (a) At 1 300 °C, the sample An_{70} is still in the solid-only field (Figure 16) and therefore consists of crystals of An_{70}.

(b) The solidus.

(c) The first liquid appears when the sample (An_{70}) intersects the solidus. This happens close to point d in Figure 16, at a temperature of 1 390 °C. The liquid plots on the liquidus and at 1 390 °C its composition is about An_{33}.

(d) At 1 450 °C, the total sample plots in the solid-and-liquid field and therefore contains both crystals and liquid.

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(e)   At 1 450 °C, the crystals are An_{81} (on the solidus) and the liquid is An_{52} (on the liquidus).

(f)   The last crystals disappear when the total sample (An_{70}) crosses the liquidus. This occurs at 1 490 °C, where the composition of the (last) crystals is An_{89}.

(g)   At 1 600 °C, the sample is in the liquid-only field and is therefore entirely liquid.

SAQ 9   This answer is illustrated in Figure 72. At 1 600 °C, the sample of Fo_{30} plots at point a on Figure 72. When it is cooled to 1 400 °C, it has moved to point b and plots in the solid-and-liquid field—the crystals plot on the solidus (point C) and the liquid plots on the liquidus (point L) at the same temperature. Thus the crystals have composition Fo_{45} and the liquid is Fo_{15}.
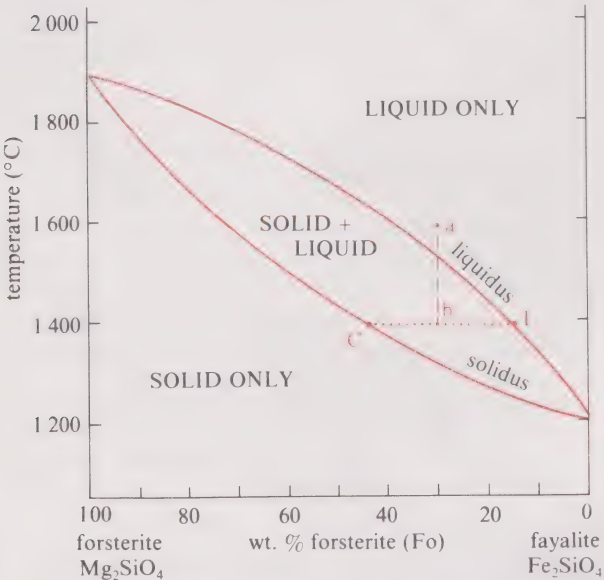
FIGURE 72   Answer to SAQ 9.

From the text (and Figure 17),

$$\text{percentage of crystals} = \frac{Lb}{LC} \times 100$$

from Figure 17, Lb = 10 mm and LC = 20 mm. Hence,

$$\text{percentage of crystals at 1 400 °C} = \frac{10}{20} \times 100$$
$$= \frac{1}{2} \times 100$$
$$= 50 \text{ per cent}$$

SAQ 10   (a)   The diagram of temperature against composition for olivines (Figure 20) illustrates that crystals formed (that is, on the solidus) at different temperatures have different compositions. Therefore the variable forsterite content of the olivine crystals in Figure 27 suggests that they crystallized at different temperatures.

(b)   The crystals that have higher Fo contents formed at higher temperatures—100 per cent forsterite has a higher melting point than fayalite in Figure 20.

(c)   If a liquid is being cooled, we may assume that the crystals that formed at the higher temperature formed first. These are the crystals with the higher Fo contents, which are situated lower in the intrusion.

(d)   At 1 000 m, the Fo content of the crystals is approximately Fo_{55} (Figure 27). From Figure 20, Fo_{55} is on the solidus at a temperature of 1 470 °C, which is the best estimate of the temperature of crystallization.

(e)   In general, we have seen that when we add more components to systems (for example, NaCl to H_2O), we lower the solidus and liquidus temperatures. Our temperature estimate from (d) is therefore probably too high.

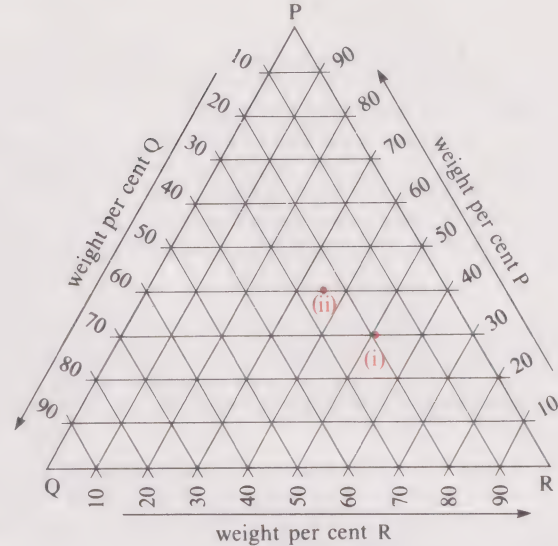**SAQ 11**   The answers are illustrated in Figure 73.

FIGURE 73   Answer to SAQ 11.

(i)   See Figure 73.

(ii)   200 g P, 125 g Q and 175 g R total 500 g, and the weights of P, Q and R must be recalculated as percentages of the total.

For P, $\frac{200}{500} \times 100 = 40$ per cent

For Q, $\frac{125}{500} \times 100 = 25$ per cent

For R, $\frac{175}{500} \times 100 = 35$ per cent

These are plotted in Figure 73.

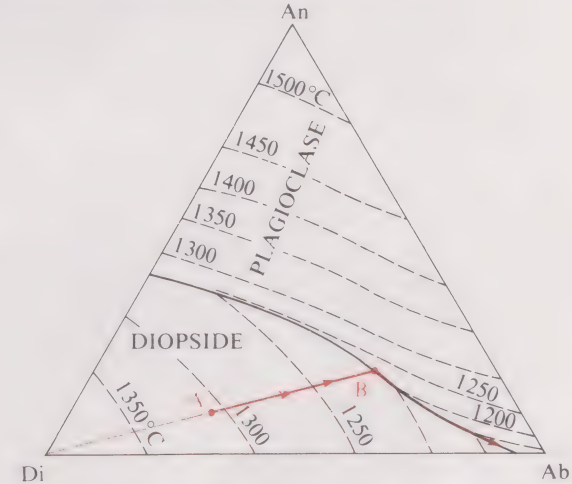**SAQ 12**   The answers are illustrated in Figure 74.

FIGURE 74   Answer to SAQ 12.

(a)   If you plot the liquid composition of 60 per cent diopside, 30 per cent albite and 10 per cent anorthite in Figure 25, it plots at point A (Figure 74). The temperature on the liquidus surface at that composition is 1 310 °C, which is therefore the temperature at which the first crystals appear.

(b)   Since this sample plots in the diopside field, the first crystals are of diopside.

(c)   As diopside crystallizes, the composition of the liquid is driven away from the diopside apex until it intersects the cotectic curve at B (Figure 74). The position of B is determined by drawing a straight line from the diopside apex through the composition of the sample (A) until it intersects the cotectic curve. This point B is where the second mineral (plagioclase) starts to crystallize and the temperature is about 1 220 °C.

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(d) While the two minerals (diopside and plagioclase) crystallize together, the liquid moves down the cotectic curve from B towards the albite–diopside eutectic.

(e) Assuming that complete equilibrium is maintained throughout crystallization, the composition of the last plagioclase crystals will be the same as that in the original liquid, that is, An_{25} (25 per cent anorthite, 75 per cent albite). (*Note* Although you were not asked specifically to do so, you could estimate the approximate temperature (less than 1 150 °C) and composition of the final liquid (An_{2-5}) from the liquidus and solidus curves for compositions on the cotectic curve projected onto the Ab–An face of the model in Figure 24.)

SAQ 13 (a) In the Di–Ab–An system (Figures 24 and 25), the cotectic curve slopes down-temperature from the Di–An to the Di–Ab eutectic. Thus, non-equilibrium crystallization, which produces lower-temperature liquids, drives them towards the Di–Ab eutectic.

(b) Anorthite contains much more CaO than albite (see Table 3), and thus liquids driven towards the Di–Ab eutectic by non-equilibrium crystallization will be *poorer* in CaO than those generated by equilibrium crystallization.

(c) Anorthite and diopside both contain less SiO_2 than albite (Table 3). Thus, since the liquid at P (Figure 25) contains more anorthite and diopside than a liquid at the Di–Ab eutectic, it must also be *poorer* in SiO_2.

SAQ 14 The SiO_2 and Al_2O_3 contents of selected volcanic rocks from Jebel al Abyad (Table 6) are plotted in Figure 75. Note that the various letters and lines related to them are for the answers to SAQs 15–17.

(a) The trend of the samples of volcanic rocks in Figure 75 is not straight—rather, there is a marked change in slope (a kink) at 58–60 per cent SiO_2 and at about 18 per cent Al_2O_3.

(b) A change of slope in the trend of results on chemical variation diagrams such as Figure 75 signifies that a new mineral has started to crystallize and, either on its own or with other minerals, has taken control of the chemical evolution of the liquid.

(c) (i) From 47 per cent to about 58–60 per cent SiO_2, Al_2O_3 increases with increasing SiO_2. Assuming that this reflects fractional crystallization, the mineral extract must have less Al_2O_3 and SiO_2 than the liquid at 47 per cent SiO_2.

(ii) From about 60 to 73 per cent SiO_2, Al_2O_3 decreases with increasing SiO_2; thus the extract must have *more* Al_2O_3 but *less* SiO_2 than the liquid at 60 per cent SiO_2.

SAQ 15 The SiO_2 and Al_2O_3 contents of the minerals in Table 7 are plotted in Figure 75. None of these minerals plots on the extension of the trend of the volcanic rocks with 47–56 per cent SiO_2 and we may conclude that the crystallization and separation of any *one* mineral could *not* by itself have controlled the chemical evolution of these rocks.

SAQ 16 (a) If the crystallizing assemblage (the extract) consists only of olivine and plagioclase, it must lie on the line connecting those two minerals in Figure 37 (see also Figure 31a). Since the extract must also lie on the extension of the trend of the volcanic rocks, it must plot at point E in Figure 75. E, the extract, therefore has 15.5 per cent Al_2O_3 and 45.5 per cent SiO_2.

(b) From Figure 75 the distance E to plagioclase = 70 mm, the distance E to olivine = 66 mm, and thus the distance olivine to plagioclase = 66 + 70 = 136 mm. The distances between E and olivine and between E and plagioclase are nearly the same, and so the proportions of each mineral must be approximately 50:50. But the E–olivine distance is slightly *less* than E–plagioclase, so there will be slightly *more* olivine than plagioclase.
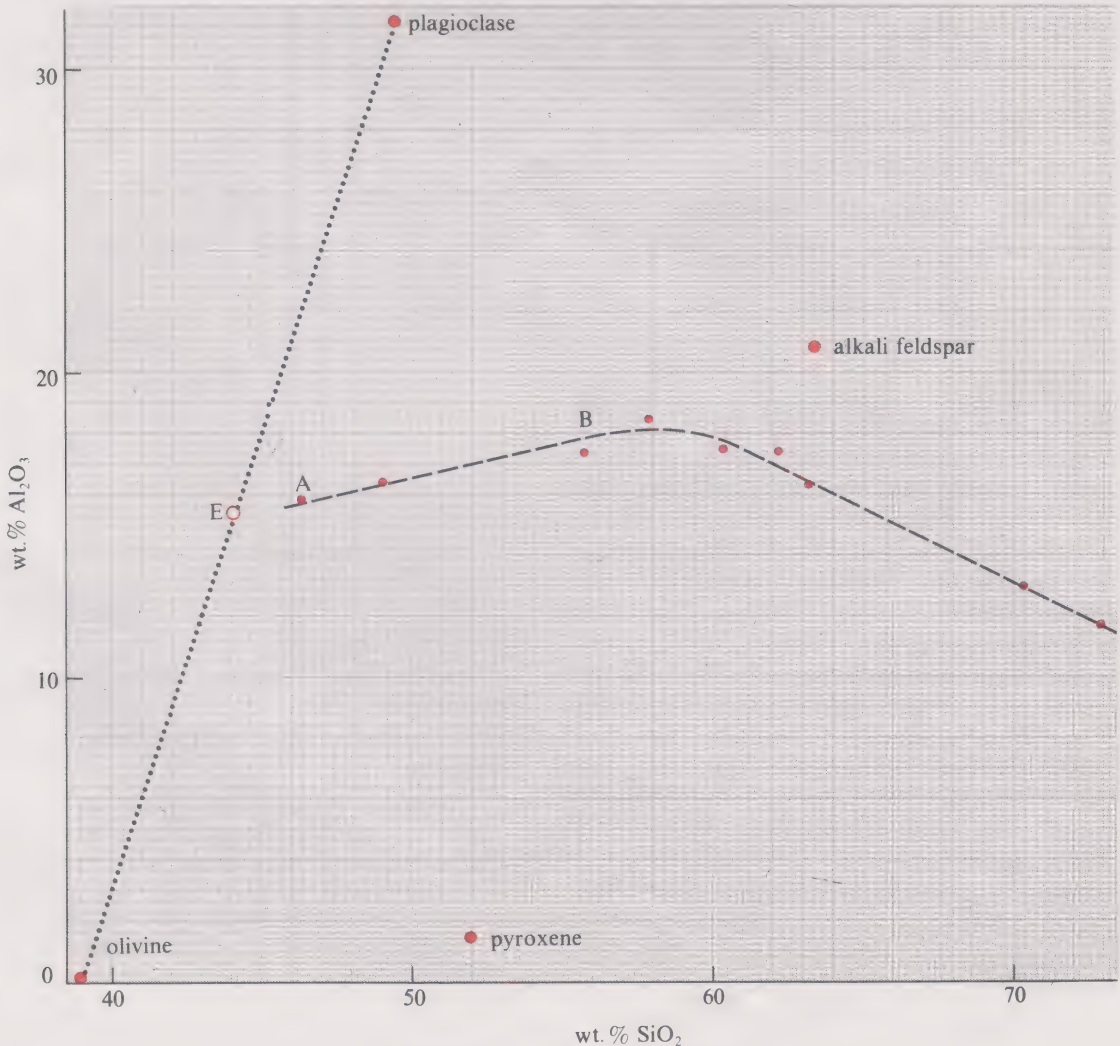
Using the mixing calculation,

FIGURE 75 Answers to SAQs 14–16.

weight per cent of plagioclase $= \dfrac{100 \times (\text{E–olivine})}{(\text{olivine–plagioclase})}$

$= \dfrac{100 \times 66}{136}$

$= 48.5$

The extract E therefore consists of 48.5 per cent plagioclase and 51.5 per cent olivine.

(c)   If the liquid at 47 per cent SiO_2 is A and that at 56 per cent SiO_2 is B (Figure 75), then EA = 12 mm, AB = 38 mm and EB = 50 mm.

Using the mixing calculation,

weight per cent of $E = \dfrac{100 \, AB}{EB}$

$= \dfrac{100 \times 38}{50}$

$= 74$

Therefore 74 per cent crystallization of the extract E (that is, olivine and plagioclase) is required to drive the liquid from 47 per cent to 56 per cent SiO_2.

SAQ 17   (a)   In the rocks with less than 58 per cent SiO_2, Al_2O_3 increases as SiO_2 increases.

(b)   The kink (at 58–60 per cent SiO_2) in the trend of the analyses you plotted on Figure 37 signifies a change in the minerals that are controlling the evolution of the liquids. For liquids above 60 per cent SiO_2, Al_2O_3 *decreases* as SiO_2 increases, and thus the extract must contain *more* Al_2O_3 than the liquid.

(c)   The feldspars (plagioclase and alkali feldspar) both contain more Al_2O_3 than the liquids and crystallization of feldspar must become increasingly important in these high-SiO_2 rocks.
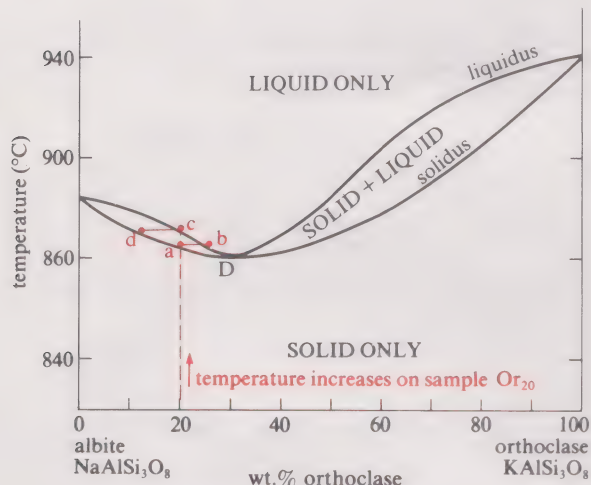
SAQ 18   The answers are illustrated in Figure 76.

FIGURE 76   Answer to SAQ 18.

(a)   As the temperature increases, sample Or_{20} intersects the solidus at 864 °C (point a). This is the temperature at which the first liquid appears and it plots on the liquidus at that temperature (point b). The composition of the first liquid is therefore Or_{26}.

(b)   The last crystals are present as the total sample plots on the liquidus—as it moves from the solid-and-liquid field to the liquid-only field. This is at point c and the crystals are on the solidus at that temperature (point d). The temperature is therefore 870 °C and the composition of the last crystals is Or_{13}.

SAQ 19   The answers are illustrated in Figure 77.

(a)   The sample consisting of 20 per cent quartz, 70 per cent albite and 10 per cent orthoclase plots in the alkali feldspar field at point L. Therefore the first mineral to crystallize is alkali feldspar.
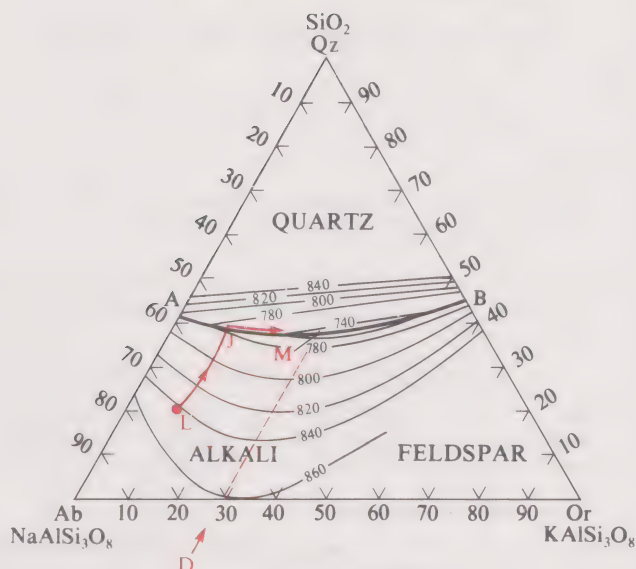

FIGURE 77   Answer to SAQ 19.

(b)   This sample plots on the albite-rich side of the feldspar minimum (the line DM on Figure 42). The phase diagram for the pure Ab–Or system (Figure 39) therefore illustrates that the first crystals have more albite and thus *less* orthoclase than the co-existing liquid.

(c)   The first crystals appear at 845 °C.

(d)   If equilibrium is maintained throughout crystallization, the feldspar becomes richer in orthoclase as the temperature falls (see Figure 39).

(e)   If zoned feldspar crystals form, the centres consist of the higher-temperature mineral and in this sample they are therefore richer in albite.

(f)   Crystallization of the alkali feldspar, which we have argued will be richer in albite than the liquid, drives the liquid towards the cotectic along a path which is curved because the crystallizing feldspar is becoming richer in orthoclase. At the cotectic the first crystals of quartz appear at a temperature of about 775 °C (at J).

(g)   No, because crystallization will cease when the composition of the feldspar crystals is the same as those in the original sample, approximately $Or_{12.5}$.

SAQ 20   In the discussion of Figure 38, we suggested that two major problems with the fractional crystallization model were that (a) 60–70 per cent fractional crystallization was probably necessary and the resulting large quantity of crystals has not been found, and (b) basaltic liquid probably represents 20 per cent partial melting of peridotite and thus large volumes of mantle are required to produce reasonable quantities of granitic magma.

SAQ 21   (a)   For Sr distributed between plagioclase (225 p.p.m.) and groundmass (100 p.p.m.) crystals, the partition coefficient K_D is given by

$$K_D = \frac{\text{concentration of Sr in plagioclase}}{\text{concentration of Sr in groundmass (liquid)}}$$

$$= \frac{225}{100}$$

$$= 2.25$$

(b)   From Section 7.1,

$$\text{percentage of plagioclase crystallization} = \frac{100 \, (C_1 - C_2)}{C_p - C_2}$$

where C = the concentration of Sr in the different phases; p = plagioclase (225 p.p.m.); 1 = the initial liquid (100 p.p.m.); 2 = the final liquid (75 p.p.m.).

Thus,

$$\text{percentage of plagioclase crystallization} = \frac{100\,(100 - 75)}{225 - 75}$$

$$= \frac{2\,500}{150}$$

$$= 16.7$$

So 16.7 per cent of plagioclase must crystallize to change the Sr concentration in the liquid from 100 to 75 p.p.m.

SAQ 22 (a) The *bulk* partition coefficient (D) for potassium (K) distributed between peridotite and a basaltic melt is given by equation 5:

$$D = (X_o K_D)_\alpha + (X_o K_D)_\beta + (X_o K_D)_\gamma + (X_o K_D)_\delta$$

where X_o = initial proportions of the different minerals in the peridotite expressed between 0 and 1; olivine = 0.6, orthopyroxene = 0.18, garnet = 0.12, and clinopyroxene = 0.10;

K_D = partition coefficient (Table 8)

α, β, γ, δ = the different minerals: olivine, orthopyroxene, garnet, clinopyroxene, respectively.

Thus D = $(0.6 \times 0.001) + (0.18 \times 0.001) + (0.12 \times 0.001)$

$\qquad + (0.10 \times 0.002)$

$= 0.000\,6 + 0.000\,18 + 0.000\,12 + 0.000\,2$

≈ 0.001

The bulk partition coefficient for potassium distributed between peridotite and a basaltic melt is 0.001.

(b) The bulk partition coefficient for potassium is 0.001 whereas that for zirconium is 0.057. Thus potassium is more *incompatible* and enters the melt more readily than zirconium, that is, the Zr/K ratio of a 10 per cent melt will be slightly *lower* than that in the original peridotite.

SAQ 23 (a) From equation 4,

$$C_1 = \frac{C_o}{D + F\,(1 - D)}$$

where C_1 and C_o are the concentration of the trace element in the liquid and the original solid respectively, D is the bulk partition coefficient (see Table 9), and F is the per cent melt expressed between 0 and 1.

Thus for Zr, after 5 per cent melting ($F = 0.05$) of garnet peridotite ($D = 0.057$ and $C_o = 8$ p.p.m.),

$$C_1 = \frac{8}{0.057 + 0.05\,(1 - 0.057)}$$

$$= \frac{8}{0.057 + (0.05 \times 0.943)}$$

$$= \frac{8}{0.104}$$

$$= 76.8$$

So, after 5 per cent melting of garnet peridotite, the concentration of Zr in the liquid is 76.8 p.p.m.

Similarly, for Y, $D = 0.332$ (Table 9), $C_o = 4$ p.p.m., and after 5 per cent melting of garnet peridotite its concentration in the liquid is 11.0 p.p.m.

The Zr/Y ratio is therefore

$$\frac{76.8}{11} \approx 7.0$$

Using the same calculation, after 15 per cent partial melting of garnet peridotite the concentrations of Zr and Y in the liquid are 40.3 and 9.3 p.p.m. respectively. Zr/Y equals $\frac{40.3}{9.3} \approx 4.3$

(b) Most ocean-ridge basalts have Zr/Y ratios of 2–3.5, whereas those from ocean-island basalts are in the range 3.5–8 (Figure 50).

Your calculations from (a) indicate that the Zr/Y ratios in ocean-ridge and ocean-island basalts could only be generated by partial melting of peridotites with the same Zr/Y ratio if: (i) the peridotites contain garnet so the bulk partition coefficient (D) for Y is much larger than that for Zr; and (ii) if ocean-ridge basalts represent *more than* 15 per cent partial melting, while ocean-island basalts represent *less than* 15 per cent partial melting. This is a contentious issue, but for other reasons, such as the differences in their Rb/Sr ratios (ITQ 28), it is most unlikely that ocean-ridge and ocean-island basalts are generated by partial melting of peridotites with similar trace-element ratios. Rather, they are likely to have fundamentally different sources.

SAQ 24 (a) The Rb/Sr ratios of the basalts are $1/100 = 0.01$ and $11/80 = 0.13$ respectively. Because plagioclase preferentially takes up Sr, the basalt with the lower Sr content and higher Rb/Sr ratio is more likely to have been derived by partial melting of plagioclase-bearing peridotite.

(b) The Rb/Sr ratio of the peridotite which on 15 per cent partial melting yields a basalt with 11 p.p.m. Rb and 80 p.p.m. Sr is obtained from equation 4 as follows:

$$C_1 = \frac{C_o}{D + F\,(1 - D)}$$

For Sr, $\qquad 80 = \dfrac{C_o}{0.272 + 0.15\,(1 - 0.272)}$

Therefore $\qquad C_o = 80\,[0.272 + (0.15 \times 0.728)]$

$\qquad\qquad\quad = 30.5$ p.p.m.

For Rb, $\qquad 11 = \dfrac{C_o}{0.085 + 0.15\,(1 - 0.085)}$

Therefore $\qquad C_o = 11\,[0.085 + (0.15 \times 0.915)]$

$\qquad\qquad\quad = 2.44$ p.p.m.

Therefore the Rb/Sr ratio in the original peridotite is $2.44/30.5 \approx 0.08$.

SAQ 25 The results from Table 10 are plotted in Figure 78. Five of the six points lie on a straight line; sample 5 does not. The slope of the straight line (the isochron) equals y/x.

$$x = 0.730\,5 - 0.712 = 0.018\,5$$

$$y = 2.60 - 0 \qquad = 2.60$$

Therefore $\qquad$ slope $= y/x = \dfrac{0.0185}{2.60} = 0.00712$

But the slope $= \lambda t$, and λ (the decay constant for ^{87}Rb) $= 1.42 \times 10^{-11}$/year^{-1}.

Thus $\qquad\qquad\qquad 0.007\,12 = 1.42 \times 10^{-11} \times t$

$$t = 501 \times 10^6 \text{ years}$$

The slope of the isochron in Figure 78 corresponds to an age of 501 Ma.

SAQ 26 There are three likely reasons, apart from analytical error, why sample 5 plots below the isochron in Figure 78:

(i) its age is different from that of the other samples in Table 10,

(ii) it had a different initial Sr-isotope ratio,

(iii) during the last 501 Ma, the Rb/Sr ratio has changed by some process other than that of radioactive decay, for example, chemical alteration during weathering.

SAQ 27 The initial Sr-isotope ratio of the isochron in Figure 78 is 0.712. If you plot that on Figure 57 at an age of 501 Ma, it falls on the evolution line for the sediments (ED). Thus if these rocks were samples of a 501 Ma old granite from Namibia, the evidence from their initial ^{87}Sr/^{86}Sr ratio suggests that they could have been derived by partial melting of the sediments.
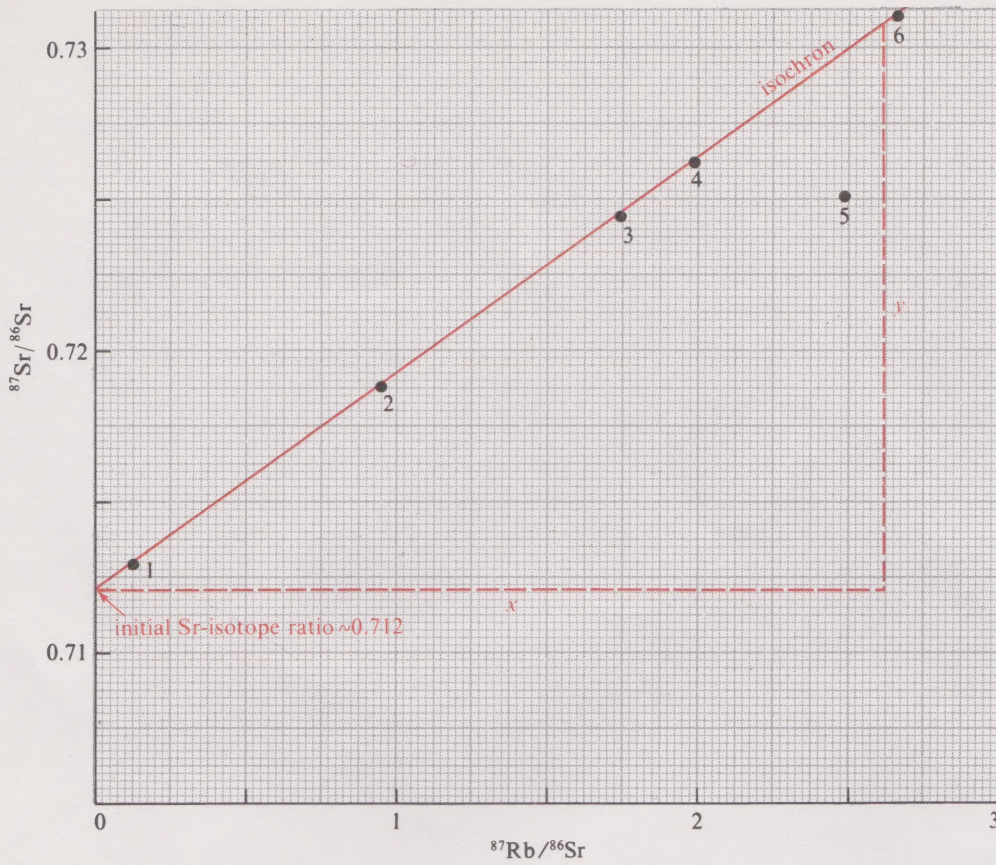
FIGURE 78 Answer to SAQ 25.

The Earth: Structure, Composition and Evolution

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